

Fundamentals of Thermodynamics

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Fundamentals of Thermodynamics

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FUNDAMENTALS OF THERMODYNAMICS
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Contents

Preface	ix
Chapter 1. Introductory Principles and Definitions	
Meaning of the Subject	1
Basis for the Laws of Thermodynamics	3
Working Medium	5
The Meaning of Temperature	5
Thermometry	6
Thermodynamic Coordinates	8
Pressure	10
Volume	12
Absolute Zero of Temperature. Charles' Law	12
Thermal Capacity and Specific Heat	14
Latent Heat	17
Chapter 2. Heat and Work	
The First Law of Thermodynamics	19
Exact Meaning of the Word "Heat"	20
Mechanical Equivalent of Heat	22
Intrinsic Energy	23
Kinetic Theory Explanation of Intrinsic Energy	24
The Conservation of Energy. Bernoulli Equation	25
Conditions Under Which the Bernoulli Equation Is Applicable	26
Steady-Flow Processes	27
Non-Flow Processes	28
General Energy Equation of Thermodynamics	28
Algebraic Sign Convention for Terms of the General Energy Equation	31
Enthalpy	31
Energy Equation for Non-Flow Processes	36
Limiting Types of Thermodynamic Changes	37
Point and Path Functions	37
Evaluation of ${}_1Q_2$	42
Evaluation of ${}_1W_2$	43
Work Done in Cyclical Processes	46
Indicator Cards	47

Chapter 3 Availability of Heat Energy

Reversibility	53
The Carnot Cycle	55
The Carnot Principle	59
Thermodynamic Scale of Absolute Temperature	62
Factors Affecting Carnot Efficiency	64
✓ The Second Law of Thermodynamics	65
Entropy	67
Summary of the Properties of Entropy	76
Use of Entropy	77
Entropy Change in Irreversible Processes	79
Use of Point Functions in Evaluating ${}_1Q_2$ and ${}_1W_2$	83
The Gibbs Helmholtz Equation — Determination of ΔH and ΔF	93
Dependence of ΔE , ΔH , and ΔF on Temperature The Third Law of Thermodynamics	97

Chapter 4 Thermodynamic Properties of Gases, Gaseous Change of State

Introduction	105
Boyle's Law	105
Charles' or Gay Lussac's Law	106
Ideal Gas Law	107
Constant Volume Gas Thermometer	110
Units	111
The Gas Constant	112
Application of the Ideal Gas Law	113
Other Characteristic Equations	114
Critical Pressure, Volume, and Temperature	117
Compressibility Factors	118
Variable Specific Heats of Gases	120
Gaseous Mixtures	126
Specific Heat of Gaseous Mixtures	128
Joule's Law	129
Joule Thomson Effect	131
Linde Process for the Liquefaction of Gases	133
Gaseous Change of State	135
Non Flow Constant Volume Change of State of a Perfect Gas	135
Non Flow Constant Pressure Change of State of a Perfect Gas	140
Non Flow Isothermal Change of State of a Perfect Gas	143
Non Flow Adiabatic Change of State of a Perfect Gas	146
Non Flow Polytropic Change of State of a Perfect Gas	150

Chapter 5. Thermodynamic Properties of Vapors, Vapor Change of State

Nature of a Vapor	161
Characteristic Equations of Vapors	161
Properties of Water Vapor	162
Clapeyron Equation	163
Clausius-Clapeyron Equation	164
The Steam Tables	167
Physical and Graphic Interpretation of Steam Tables	172
The Mollier (h) Diagram	176
Change of State of Water Vapor	177
Non-Flow Constant-Volume Change of State of Water Vapor	178
Non-Flow Constant-Pressure Change of State of Water Vapor	180
Non-Flow Isothermal Change of State of Water Vapor	182
Non-Flow Adiabatic Change of State of Water Vapor	186
Non-Flow Polytropic Change of State of Water Vapor	187
Constant-Enthalpy Change of State of Water Vapor (Throttling Process)	190
The Throttling Calorimeter	193
Limitations of the Throttling Calorimeter	194

Chapter 6. Compressed Air

The Use of Compressed Air	200
The Ideal Compressed Air Cycle	201
Work of the Compressor	203
Source of Work Done by the Cycle	205
Water Jacketing	207
Multi-Stage Compression	209
Volumetric Efficiency. Clearance	210
The Air Engine	214
Reheating	215
Overall Efficiency of the Compressed-Air Cycle	216

Chapter 7. Internal Combustion Engines, The Otto and Diesel Cycles

Early Developments	218
The Otto Cycle	220
The Diesel Cycle	221
Methods of Computing Efficiencies of Internal Combustion Engines	222
Indicated Power and Brake Power	223
Air Standard Analysis	225
The Ideal Four-Stroke Otto Cycle	226
Air-Standard Efficiency, Otto Cycle	226
The Ideal Four-Stroke Diesel Cycle	230

Air Standard Efficiency, Diesel Cycle	231
Theoretical Analysis of Internal Combustion Engine Cycles	235
Empirical Formulas	236
Chapter 8 Steam Cycles, Steam Engines and Turbines	
Introduction	239
Equipment of the Steam Power Plant	240
The Ideal Rankine Cycle	241
Methods of Improving Rankine Efficiency	246
Decreasing the Condenser Temperature	246
Superheating	247
Increasing the Boiler Pressure	249
Improvements in Efficiency Outside the Rankine Cycle	251
Regenerative Feed Heating Cycle	252
Reheating and Reheating Regenerative Cycles	254
Binary Cycles	255
The Reciprocating Steam Engine	257
The Incomplete Expansion Cycle	259
Engine Governing	262
Turbines	262
The Expansion of Steam Through a Nozzle	263
The Impulse Turbine	265
Pressure Staging Impulse Turbine	267
Velocity Staging Impulse Turbine	267
Reaction Turbines	267
List of Symbols	272
Steam Tables	274
Index	283

Preface

In writing this book, the authors sought to make its scope broad enough to give the beginning student an understanding of the fundamentals of thermodynamics adequate for further related study in mechanical engineering, physics, and chemistry.

It is the authors' firm conviction that every beginning student of thermodynamics must have an understanding of the subject as a whole before he can effectively apply its principles in the field of his specialty. Specialization at the beginning of the study of a subject makes the knowledge gained vocational rather than professional in character.

The methods of thermodynamics have proved so useful in the fields of their application that specialized textbooks on the subject, are conventionally differentiated by titles like Engineering Thermodynamics, Thermodynamics for Chemical Engineers, and Chemical Thermodynamics.

The authors believe that it is unfortunate that this differentiation and specialization have extended to the beginning level of instruction. Inevitably, this has led to the mechanical engineering student often being entirely unaware of the applications of thermodynamics to chemistry and physics, or, at least, coming to the stultifying conclusion that the thermodynamics he is studying has nothing in common with that of his fellow student in chemistry. The converse has been equally true. Surely, the principles of thermodynamics are of such broad fundamental significance to all scientific and engineering endeavor that their study should not be partitioned in terms of their applications at the beginning.

In presenting the subject matter, emphasis has been constantly and deliberately placed on a straightforward approach on the solid foundation of the laws of thermodynamics themselves. The authors, like other teachers of the subject, have found that many sincere students are easily confused when the subject is introduced via the gas laws or the kinetic theory of gases. While it is true that the latter approaches excite the student's natural interest in "what makes the wheels go round," they also give him a wrong first impression of the overall statistical considerations of energy exchange that characterize the subject. Once this first impression has been made, it is exceedingly difficult to correct.

Hence the authors have introduced, at the beginning, the thought that thermodynamics is first concerned with energy and have endeavored to make it clear that, in order to determine energy exchange, consideration must then be given to the state of the thermodynamic medium. It is sincerely hoped that no student of this book will ever come to the conclusion that the laws of Boyle and Charles are basic *thermodynamic* laws.

In their work the authors have had recourse to many of the excellent books on the subject. They have also received invaluable assistance from their colleagues and from those who have used the mimeographed version of the text in their classes. So various are these sources of assistance that it is impossible to give adequate acknowledgment to them all within the compass of this preface. Special mention must be made, however, of the helpful comments and suggestions made by L. M. K. Boelter and A. R. Collins. The authors are likewise indebted to Samuel Shulits, George W. Thomas, Kenneth E. Rose, and Van W. Donohoo, who used the text in the classroom in mimeographed form and made many valuable suggestions for its improvement. The authors' thanks go also to Mr. Donohoo for the preparation of a revised mimeographed edition which he used successfully in an E S M W T* course. The difficult task of editing the final draft of the manuscript for printing was undertaken by Louis D. Conta, who has also given much assistance in the reading of proof. Finally, the authors wish especially to thank Violet Horning and Dorothy Adams for their patience and accuracy in typing the several drafts of the manuscript which have been made.

A. S. ADAMS
G. D. HILDING

Fundamentals of Thermodynamics

Introductory Principles and Definitions

Meaning of the Subject

At the beginning of the study of any phase of knowledge, the student very properly wants to know the answers to two questions. The first is: How does the new subject relate to knowledge gained previously? The second is: What are the general concepts to be learned in the new field of study?

In thermodynamics the clue to the answer to the first question is to be found in the prefix "thermo," which comes from the Greek word meaning "heat." The prefix is significant, for thermodynamics was originally called the dynamical theory of heat. Clearly, then, the subject is closely related to that part of physical science called heat. The suffix "dynamics" also has bearing on the relation of the subject to other fields of knowledge. When the word thermodynamics was coined in the middle of the last century, "dynamics" was taken to refer both to considerations of energy and to the behavior of bodies acted upon by forces. Today "dynamics" generally has only the latter meaning, *except in thermodynamics* where it definitely refers to energy. Evidently, thermodynamics is also related to the older science of mechanics, in which the mechanical energy of bodies is studied. From what has already been said concerning the meaning of the parts of the word, we are in a position to understand readily the meaning of the whole. A satisfactory definition is that *thermodynamics is that branch of physical science that treats of the relation between heat and other forms of energy.*

The importance of the study of this relation is seen when we consider that the tremendous industrial development of the present has been largely accomplished by the application of thermodynamic laws. Modern civilization is characterized by the utilization of power rather than by the use of human labor and drudgery. In every instance the source of the power may be ultimately traced back to heat energy. Hence, if we are to understand modern life we must know something concerning the way in which heat energy is transformed to develop power. As an example, consider the automobile, which has so pro-

foundly influenced our manner of living. Everyone knows that in the automobile engine gasoline vapor is burned, or exploded, in the cylinders. As a result of the burning, mechanical energy is supplied to the driving wheels, and the vehicle moves. Thermodynamics is concerned with the details of the manner in which the heat energy derived from the burning of the gasoline is transformed into the mechanical energy that turns the wheels. Examples of this type could be multiplied almost indefinitely. All of them show that man's control over his environment, resulting in his greater comfort and convenience, comes primarily from the efficiency with which he converts heat energy into mechanical energy or work.

Originally the study of thermodynamics was confined to the relation between heat and mechanical energy, but later its scope was extended to include transformations of heat to other forms of energy, or vice versa. In particular, the study of the relation between heat and chemical energy has proved fruitful, and thus the science of chemistry is related to that of thermodynamics. Yet another fundamental science is related to the subject at hand, and in order to show its relationship we must look at the manner in which thermodynamics developed. Perhaps the outstanding characteristic of thermodynamics is that, speaking generally, a great number of physical and chemical laws have been deduced by logical reasoning from *only two broad principles*. The formulation of logical reasoning is best accomplished through the agency of the science of mathematics. So it is that the answer to our first question is that thermodynamics is a part of the science of physics and chemistry and is intimately related to mathematics.

The answer to the second question is indicated to some extent by the answer to the first. Evidently, if thermodynamics treats of the relationship between heat and other forms of energy, the fundamental principles of the subject will be the physical laws governing that relationship. As is true in two other great branches of physical science, mechanics and electrodynamics, the number of underlying physical laws in thermodynamics is very small. Indeed, in the so-called "classical" thermodynamics there are but two basic principles, conveniently designated as the First and Second Laws of Thermodynamics. In comparatively recent years considerable evidence has been brought to light, principally by chemists, to show the validity of a third underlying principle or law. From these three principles or laws an astonishingly large number of far-reaching conclusions have been drawn. It follows that a study of the subject is a study of this development, to the end that the student may gain a lively appreciation of the significance of the fundamental laws.

Basis for the Laws of Thermodynamics

At the outset it must be understood that the laws of thermodynamics are empirical; that is, they have been established by the evidence of an almost countless number of experiments. Further, in their development, *no* assumptions are made as to the nature of heat or the structure of matter. In order to understand the principles better, it may help the student to consider the modern theories of heat and matter; but he should keep in mind that so far as thermodynamics is concerned, the laws take account only of *directly measurable* quantities such as pressure, volume, temperature, quantity of heat, and the like.

The First Law had its origin in the experiments of Count Rumford, an American Tory, who was forced to leave the United States because of the Revolution. He entered the service of the Elector of Bavaria as an armorer, in which capacity he had charge of a gun factory. He noticed that as the guns were bored a great deal of heat was manifested, and his curiosity about this phenomenon led him to make experiments to determine its cause.

He found that the boring chips possessed the same properties as the block metal, a result which proved that the heat was not a property peculiar to the form of the metal. Another possibility he considered was that the heat might have come from some sort of chemical reaction of the metal with the atmosphere. In order to test this, he bored cannon under water and found that the same amount of heat was liberated as before. From the result of these and other experiments he announced his conclusion in 1789 that the heat came from the mechanical work expended in boring the cannon. Subsequent experiments by Sir Humphry Davy, Robert Mayer, and particularly those performed from 1830 to 1843 by James Prescott Joule gave such conclusive evidence that in 1847 Helmholtz published a famous paper asserting the principle of conservation of energy and the equivalence of heat and mechanical energy. The evidence was so conclusive that the principle was accepted by the scientific world and became known as the First Law of Thermodynamics. *A simple statement of the law is that heat is a form of energy that can be transformed into other forms of energy, but since energy can neither be created nor destroyed the total amount of energy in any transformation remains constant.* Everyone has observed a manifestation of the First Law in the heating of automobile brakes. If careful measurements were made and the friction of mechanisms other than the brake system subtracted, it would be found that the decrease in the total energy of motion and position of the car is exactly equivalent to the heat developed at the brake bands.

In 1824 Sadi Carnot, a young French engineer, became interested in devising means for improving the efficiency of the steam engine, which had been invented by Watt some fifty years before. Carnot thought that perhaps some other medium than water vapor might give the desired improvement in efficiency, but as a result of his studies he found that the nature of the medium had nothing to do with the efficiency of the engine. The inherent characteristic of any heat engine is that heat is supplied at a relatively high temperature, some of it is converted into work by the processes in the engine and the remainder leaves the engine in the exhaust at a relatively low temperature. Carnot deduced that the efficiency of a heat engine operating between two given temperatures depended on those temperatures and on the reversibility of the changes that took place in the engine. Carnot's work was revised and extended by Lord Kelvin in 1851, with the conclusion that the measure of the transformation of heat energy into mechanical energy in any heat engine is in the temperature of the heat supply and rejection and in the reversibility of the process. This conclusion means that *heat energy is available for transformation into mechanical energy only to the degree that its temperature is above the lowest attainable temperature to which the engine can reject its exhaust*. Hence, no heat energy can be transformed into mechanical energy if its temperature is at or below the lowest temperature of the surroundings. Thus, while the First Law tells us that heat energy is always equivalent to mechanical energy, the Second Law limits the extent to which the transformation can actually be made. Perhaps the best statement of the Second Law was given by Clausius, "*It is impossible for a self acting machine, unaided by external agency, to convey heat from one body to another at a higher temperature, or heat cannot by itself (i.e., without having work done) pass from a colder to a warmer body*."

An illustration of the application of the Second Law is given by considering the energy in the oceans of the world. Since the average temperature of all oceans is about 4°C , a stupendous amount of energy above absolute zero is stored in them. But none of this energy can be transformed into useful mechanical energy because there is no naturally lower temperature to which the heat can flow.*

The first two laws of thermodynamics have been the basis for the development of classical thermodynamics, in which is included all of

* A French engineer, Georges Claude, has in the last few years attempted to realize the transformation of *some* of the energy in the oceans by building a pipe from the surface of the sea to a depth of a mile or more. The temperature of ocean water at this depth is considerably less than that at the surface and so it is possible to transform a *very small part* of the energy in the water at the surface into mechanical energy. The difficulties and expense of the construction and maintenance of this apparatus have thus far been so great as to make doubtful the success of the scheme.

what is sometimes known as engineering thermodynamics. Anyone with even a slight knowledge of chemistry has observed that some chemical reactions give off heat and others require heat to cause the reaction to take place. Evidently the relation between heat energy and chemical energy should be a fruitful field of study for chemists. They have seen the possibilities of this study and a great deal of valuable information has been gained from their researches. In particular, the principle known as the Third Law of Thermodynamics, which is still somewhat in the process of development, has been the result of their studies.

The Third Law of Thermodynamics, first brought forward by Nernst, is concerned with the thermal properties of pure chemical substances at a temperature of absolute zero. Because its statement involves words and ideas which have not yet been defined in this book, discussion of it and of its significance will be deferred to a later chapter. For the present, it will be profitable for us to define and discuss in some detail the quantities and factors involved in the first two laws and the significance of the conclusions that can be drawn from them.

Working Medium

In general, the addition of heat to any substance will produce a change in its pressure, volume, and temperature. It is by means of the volume changes produced that a heat engine is able to do work or to have work done upon it. It is therefore essential that attention be given to the properties of the substance that is acting as a vehicle for the absorption or rejection of heat and for doing work. This substance is known as the *working medium*. Examples of working media are common; e.g., steam is the working medium in a steam engine plant, and the gaseous mixture made up of the products of the combustion of gasoline is the working medium in the ordinary internal combustion engine.

The Meaning of Temperature

If we place a vessel of water over a fire, we say that the water becomes hot from the heat that has been added to it. Perhaps we may try to determine its degree of hotness by putting our hand in it. But our judgment, based on sensation alone, is most capricious, for nearly the same sensations are produced by an extremely hot body as by an extremely cold one. If blindfolded, a person cannot tell whether his hand is being burned by a red-hot iron or frozen by a bit of carbon dioxide snow. The sensations are bound to be the same, for they are both induced by the physiological sensation of injury to tissue. Because

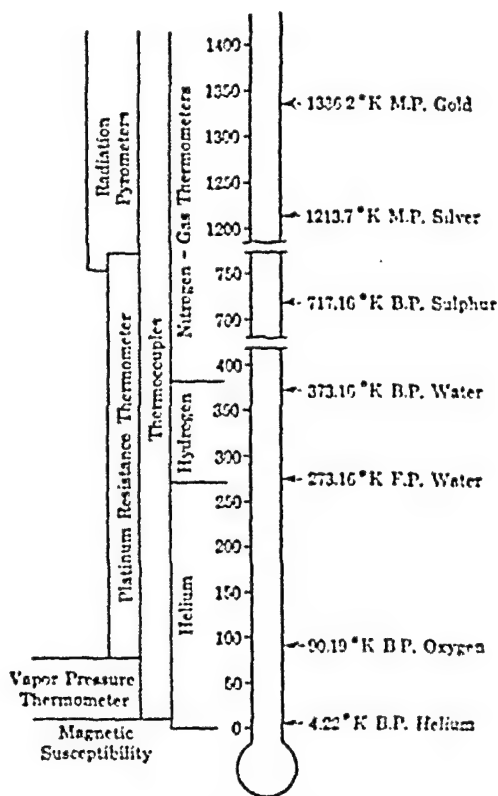
of this gross inaccuracy in the detection by sensation of the degree of hotness of a body, some objective measure is vitally necessary to a determination of the actual facts. Such a measure is given by the thermometer, by means of which we can determine which of two bodies is hotter by measuring the temperature of each. It must be kept in mind that temperature differs from a measurable quantity like a length in that when two bodies of different temperatures are mixed, the resulting temperature is not in general the sum of the two original temperatures. Moreover, although temperature indicates the relative hotness of a body, a condition caused by the addition of heat, *temperature and heat must not be confused*. Heat is a form of energy, whereas temperature is only an indication of what has happened to a body by reason of the addition or withdrawal of energy. As we shall see presently, the addition of the same quantity of heat to two different bodies at the same initial temperature generally results in different temperatures for the two bodies.

Thermometry

The addition or withdrawal of energy produces several well known changes in the properties of a body. A thermometer is a device that uses one of these changes to measure relative temperature in terms of an arbitrary scale. Probably the most common effect employed in thermometry is expansion, as exemplified in the ordinary mercury in-glass thermometer. Other effects frequently used are change in electrical resistance, and the production of an electromotive force at the heated junction of two dissimilar metals. The common mercury in-glass thermometer is generally used for ordinary purposes, but it is subject to inaccuracies that limit its usefulness for exact scientific work. Further, its range is limited to the freezing and boiling points of mercury, hence temperatures higher or lower than these must be measured by the expansion effect using other media than mercury, by the change in resistance in the resistance thermometer, or by the thermoelectric effect in the thermocouple. High temperatures are also measured by the optical pyrometer, a device which employs the principle that the amount of radiant energy at a fixed wave length emitted by a hot body is dependent upon the temperature of the body (Fig 1-1).

Before the adoption of mercury as a thermometric substance, other liquids, notably alcohol, were used in expansion thermometers. Alcohol, however, boils at a temperature lower than that for water and so its general usefulness is seriously curtailed. Moreover, the underlying disadvantage of all liquid thermometers is the fact that the expansion of

liquids is by no means regular and the corrections which must be applied are not accurately known. But the expansion of the so-called permanent gases, like hydrogen, helium, and nitrogen, is uniform over wide ranges of temperature. Such gases can be obtained in great purity



Useful Ranges of Various
Temperature Measuring Devices

FIG. 1-1.

(From W. P. Wood and J. M. Cork, *Pyrometry*,
McGraw-Hill, 2nd ed.)

and have the further advantage that they remain gaseous down to exceedingly low temperature. Also it will be shown later that the gas thermometer may be used to indicate the absolute temperature—a decided advantage. Despite these advantages, gas thermometers cannot be generally employed even in laboratories, let alone in technical work. They have two serious disadvantages in that they are cumbersome and several corrections must be applied to the readings recorded

upon them before the actual temperature is known. Consequently, the gas thermometer finds its greatest use as a primary standard with which thermometers more convenient to use may be calibrated.

All thermometers must be calibrated in terms of some arbitrary scale, of which the Fahrenheit and the centigrade scales are in common use. The former is widely used in engineering in Great Britain and the United States, whereas the latter, a more rational scale, is commonly used in other countries and is employed exclusively in scientific work. The development of an arbitrary temperature scale began in 1660 when Hooke decided to use the freezing point of water, as indicated by a mercury thermometer, as the zero point of the thermometer scale. Some years later Fahrenheit was experimenting with a mixture of salt and ice and noted that the temperature thus attained was considerably below that of freezing water. He erroneously thought he had achieved the lowest attainable temperature and so chose it as the zero on his temperature scale. As two other fixed points on the scale he selected (1) the freezing point of water as 32°F and (2) what he thought was the normal temperature of the human being. With these fixed points it turned out that the degree was of such magnitude that the boiling point of water at normal atmospheric pressure was 212°F .

In 1742, Celsius, a Swedish physicist, devised the more rational Celsius or centigrade temperature scale, on which the fixed points are the freezing and boiling points of water at normal atmospheric pressure. The expansion of a mercury column between these two temperatures is divided into 100 equal divisions, each of which thus becomes one degree centigrade. Since the expansion of a mercury column from the temperature of freezing water to that of boiling water is 180 Fahrenheit degrees and only 100 centigrade degrees, it follows that the degree Fahrenheit ($^{\circ}\text{F}$) is $\frac{5}{9}$ the degree centigrade ($^{\circ}\text{C}$). Moreover, zero on the Fahrenheit scale is 32°F below the centigrade zero. The frequently necessary conversion of readings between the two scales can be readily made with the aid of the following relationships

$$t \text{ (in } ^{\circ}\text{C)} = \frac{5}{9}(t \text{ [in } ^{\circ}\text{F]} - 32)$$

and conversely

$$t \text{ (in } ^{\circ}\text{F)} = \frac{9}{5}(t \text{ [in } ^{\circ}\text{C]}) + 32$$

Thermodynamic Coordinates

In a superficial way we are apt to jump to the conclusion that the addition of heat to a medium will do no more than cause the temperature to rise. A little more careful thought on the matter makes us

realize that when a medium is heated in the open air, i.e., at constant atmospheric pressure, there is a volume change as well as a temperature change. On the other hand, if the volume of the medium is kept constant, both pressure and temperature rise with the addition of heat. The change in the externally measurable quantities p , v , and t therefore gives direct evidence of what has happened to the medium. Consequently, if we wish to know exactly the state of a medium with reference to its thermal condition, we determine two of the three *directly measurable* quantities, pressure, volume, and temperature. In analytic geometry we locate a point on a graph by knowledge of its coordinates. By analogy, in thermodynamics, pressure (p), volume (v), and temperature (t) are called *coordinates*, since knowledge of any two of them makes it possible to locate exactly the thermal state of a medium. Moreover, when the state of a medium is determined by fixing two of the coordinates, the third coordinate takes on a definite value that depends on the values of the fixed coordinates. In mathematical language, all this is expressed by saying that any two of the thermodynamic coordinates may be taken as independent variables and that the third is a function of them. Thus $p = f(v, t)$ expresses the functional relation among the coordinates. Here volume and temperature have been taken as independent variables. When values are assigned to them, the pressure can be calculated if the form of the function is known. The functional relation between the coordinates may be expressed equally well by

$$v = \phi(p, t)$$

and

$$t = \psi(p, v)$$

in which the symbols ϕ and ψ indicate merely a different functional form. The functional relationship between the coordinates *differs for different substances*; and since it is characteristic of the behavior of the particular substance to which it applies, it is known as the *characteristic equation or equation of state* of the substance.

It should be carefully noted in the above discussion that the word "state" does *not* refer to the molecular aggregation of a medium, i.e., whether the medium is a solid, liquid, or gas. Although the word is loosely used in this way in other connections, in thermodynamics it refers *solely* to the thermal condition of a medium as determined by the coordinates. Other evidence must be supplied to determine whether the medium is a solid, liquid, or gas. In order to avoid confusion of terms, the word "phase" will be used in this book in connection with all matters having to do with the type of molecular aggregation.

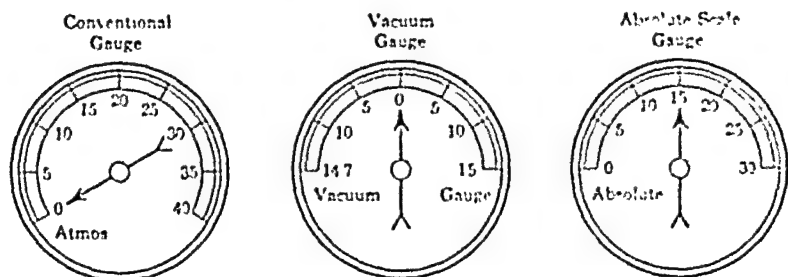
It is worth while to consider a little more fully just what is meant by

the thermodynamic state of a substance. In analytic mechanics it was learned that, relative to a certain datum, the amount of potential energy possessed by an elevated body is uniquely specified by its weight and its elevation above the arbitrarily selected datum plane. The state of the body, so far as its stored potential energy is concerned, is therefore defined by the coordinates, weight and height. Similarly, in thermodynamics, the state of a medium is defined by any two of the directly measurable quantities p , v , and t . As an illustration of what this means, suppose that we are comparing the work that can be done by a pound of compressed air under varying conditions of expansion. In order to make any intelligent comparison, the air must have identically the same properties, which amounts to saying that it must have the same energy, at the start of each expansion experiment. This is achieved by specifying its state. Any desired initial state of the air may be exactly reproduced for an indefinite series of experiments, provided that any two of the three thermodynamic coordinates are specified. For example, a pound of dry air at an absolute pressure of 100 lb per sq in. and a temperature of 60° F is perfectly definite and has the same properties at any location and at any time. Moreover, a pound of air in this state always occupies a definite volume which may be accurately computed when the functional relation $v = \phi(p, t)$ is known. The same definiteness in knowledge of the state of a substance obtains when pressure and volume or volume and temperature are used as the defining coordinates. Evidently the accurate measurement of the three quantities — pressure, volume, and temperature — is of fundamental importance. Hence, the next three paragraphs are devoted to a consideration of their units and to ordinary methods of measurement.

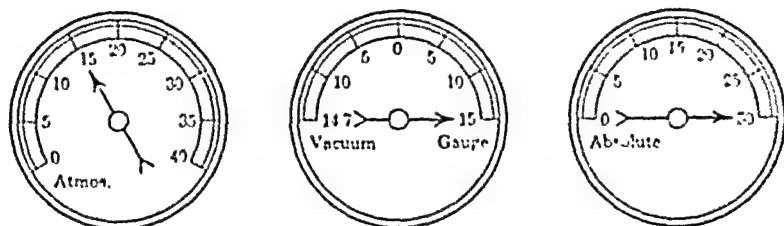
Pressure

Pressure is defined as force per unit area and is generally expressed in pounds per square inch in the British system of units, or in dynes per square centimeter or kilograms of force per square centimeter in the cgs system. It may also be expressed in terms of the height of a column of liquid, usually either mercury or water, which it will support. For conversion purposes, it is worth noting that a mercury column one *inch* high at 0° C is equivalent to a pressure of 0.4912 lb per sq in. and a water column one *foot* high at 39.3° F is equivalent to a pressure of 0.433 lb per sq in. Another unit of pressure much used for physical chemical purposes is the atmosphere, which is the pressure of 760 mm of mercury. The atmospheric pressure at sea level may be taken as being approximately equal to 14.7 lb per sq in.

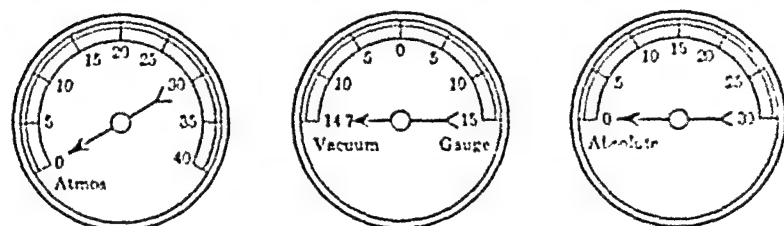
Gages for the measurement of pressure indicate the pressure above or below that of the surrounding atmosphere. If such measurements were used in thermodynamic problems it would be necessary to put a minus sign before pressures below atmospheric, a practice which would



These Gauges Are at Atmospheric Pressure



These Gauges Are Above Atmospheric Pressure



The Vacuum and Absolute Gauges are at Absolute Zero
Which the Conventional Gauge Cannot Record
FIG. 1-2. Pressure Measurements.

lead to unnecessary confusion. The difficulty is avoided by considering a perfect vacuum as zero pressure, and pressures measured relative to it as absolute pressures. This procedure has the additional advantage of simplifying the mathematical expressions for many of the thermodynamic relations to be studied later. Gage pressures can be easily converted to *absolute* pressures by the addition of the value

of atmospheric pressure (Fig 1-2) Thus, in units of pounds per square inch

$$\text{Absolute pressure} = \text{gage pressure} + \text{atmospheric pressure} \\ (14.7 \text{ lb per sq in at sea level})$$

Although gages usually indicate pressure in pounds per square inch, in thermodynamic problems it generally is necessary to convert the observed reading to units of pounds per square foot by multiplying by 144. In this book, pressure in force per unit area will be designated by p , and total pressure by P .

Volume

The volume of the material whose thermal behavior is being studied, i.e., the working medium, is the total space occupied by it. Volume is usually expressed in cubic feet in technical engineering work and in cubic meters or cubic centimeters in chemical and physical studies. In thermodynamic problems it is often convenient to deal with the specific volume, defined as the volume occupied by unit weight of the substance, e.g., cubic feet per pound. In this book v will be used to denote specific volume and V to denote the volume of M units of weight, i.e., $V = Mv$.

Absolute Zero of Temperature Charles' Law

Temperature, the third fundamental thermodynamic coordinate, is conventionally measured with a thermometer, as discussed on pages 6-8. However, since the temperatures taken as zero on both centigrade and Fahrenheit scales are wholly arbitrary values, minus temperatures commonly occur. Early in the history of thermometry physicists became interested in determining an absolute zero below which there would be no other temperature. Indeed, it is because Fahrenheit thought he had obtained absolute zero that the Fahrenheit zero has its present awkward position on the temperature scale. The advantage of establishing an absolute zero is far greater than simply the avoidance of minus temperatures. It will be shown later that many vital relationships in thermodynamics have meaning *only* when the temperature is expressed on the absolute scale.

Absolute zero may be established experimentally from measurement of the variation in the volume of a gas with change in temperature when the pressure is kept constant. In about 1787 Jacques Charles found that air and carbon dioxide both expanded the same amount for an increase in temperature of one degree. His work was later extended

and verified by Gay-Lussac and Dalton, who both found that within an accuracy of about 2% the expansion of all the simple gases was approximately the same and that the volume change per degree was equal to $\frac{1}{273}$ of the volume at 0°C . This result may be expressed as $v_t = v_0 \left(1 + \frac{t}{273}\right)$, where v_t is the volume at temperature t and v_0 is the volume at 0°C . An immediate consequence of this result is that if the pressure on a gas is kept constant and the temperature varied by the addition or withdrawal of heat, the volume change is proportional to the temperature reckoned from a zero 273°C below 0°C ; i.e.

$$v_t = \frac{v_0}{273}(273 + t).$$

It also follows that if a perfect gas were cooled from 0°C it would decrease $\frac{1}{273}$ of its volume at 0°C for each degree the temperature was lowered, until at -273°C its volume would become zero. This temperature is taken as the *absolute zero*.

Unquestionably a gas would liquefy and solidify before this temperature was reached; therefore the relationship above, obtained from

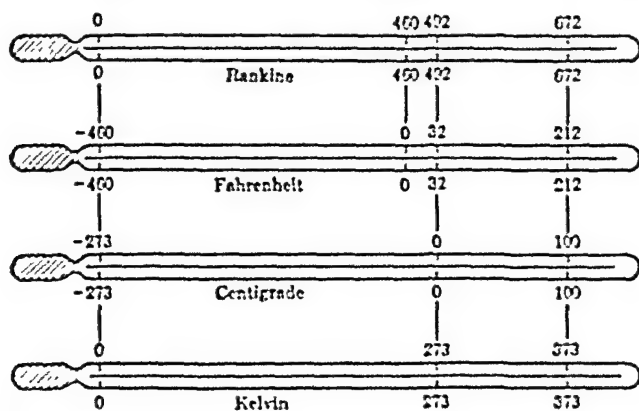


FIG. 1-3. Comparison of the Temperature Scales in Common Use in Thermodynamics.

measurements on a gas, would not apply. It is likewise impossible to conceive that matter could ever have zero volume. However, the concept of the absolute zero is valuable in that it represents an absolute limit of temperature. It will be shown later that the determination of the absolute zero of temperature is *not dependent on the properties of a gas but may be done quite independently of the properties of any material*.

Temperatures reckoned to the absolute zero are called *absolute temperatures*. The absolute scale of temperature when measured in centi-

grade degrees is called the Kelvin scale, after the English physicist of that name. Hence if absolute temperatures are denoted by T

$$T(^{\circ}\text{Kelvin}) = t(^{\circ}\text{C}) + 273$$

It is a simple matter to convert this result to Fahrenheit degrees. When expressed thus, the absolute scale of temperature is called Rankine, after the Scottish engineer. The temperature in $^{\circ}\text{Rankine}$ is given by

$$\begin{aligned} T(^{\circ}\text{Rankine}) &= t(^{\circ}\text{F}) + \frac{5}{9}(273) - 32 \\ &= t(^{\circ}\text{F}) + 460 \quad (\text{Fig. 1-3}) \end{aligned}$$

Thermal Capacity and Specific Heat

We have already seen that there is a relationship between heat and the thermodynamic coordinates in that the values of the latter are changed by the addition or subtraction of heat. Hence it is of importance to determine a standard means of expressing this relationship as well as to define the unit of heat quantity. In the early history of the study of heat and its effects, heat was thought to be a weightless fluid which was called "calor." From the introductory discussion of the First Law, we see that this idea of the nature of heat was erroneous. The error, however, does not impair the definition of the *unit* of heat given by James Black, a Scottish physician, chemist, and physicist. He defined the unit of heat as that quantity of heat which caused the temperature of one pound of water to increase by one degree. It is of importance to notice that Black associated quantity of heat with the *weight* of an arbitrary calorimetric, or heat measuring, substance. Other investigators had associated the quantity with the volumes of substances and as a result encountered wide discrepancies in their experimental results.

The unit of heat quantity expressed in British units is the *British thermal unit* (Btu), thus may be defined as the heat required to raise one pound of water one degree F. The Btu thus defined is virtually equivalent to the mean Btu which is defined as $\frac{1}{180}$ of the heat required to raise one pound of water from the freezing point to the boiling point at sea level. In the cgs system the unit is called the calorie and is defined in several ways. The most useful definition is that of the mean calorie, which is $\frac{1}{180}$ of the amount of heat required to raise the temperature of one gram of water from the freezing point to the boiling point at normal atmospheric pressure. By consideration of the relation between the units of grams and pounds and degrees C and degrees F

$$1 \text{ Btu} = 252 \text{ calories}$$

It is evident that the addition of heat to a substance will produce a change in the thermodynamic coordinates. Usually there will be a rise in temperature, but we have already seen that the value of one coordinate is not sufficient to determine the state of a substance. The value of a second coordinate must also be given. In studying the effect of the addition of heat upon a substance, this requirement is dealt with by holding one coordinate constant and measuring the ratio between the heat added and the change produced in another coordinate. This ratio is generally called the *thermal capacity*, for it shows how much heat a substance can absorb for a unit change of a coordinate. The various expressions for thermal capacity are shown below. In them q represents the heat added *per unit of weight*, and the subscript to the parentheses indicates the variable held constant.

$$\begin{array}{lll} (1) \left(\frac{q}{t_2 - t_1} \right)_p & (3) \left(\frac{q}{p_2 - p_1} \right)_t & (5) \left(\frac{q}{v_2 - v_1} \right)_t \\ (2) \left(\frac{q}{t_2 - t_1} \right)_v & (4) \left(\frac{q}{p_2 - p_1} \right)_v & (6) \left(\frac{q}{t_2 - t_1} \right)_p \end{array}$$

If the change in the variable studied is made infinitely small, these relations may be expressed

$$\left(\frac{q}{dt} \right)_p \quad \left(\frac{q}{dt} \right)_v \quad \text{etc.}$$

The first two of these ratios are especially important and are named specific heat at constant pressure (c_p) and specific heat at constant volume (c_v) respectively. Because the word *specific* implies the comparison of a certain property of a substance with the same property of an arbitrarily chosen standard substance, some authors define specific heat as the ratio of the thermal capacities $\left(\frac{q}{dt} \right)_p$ and $\left(\frac{q}{dt} \right)_v$ to the corresponding thermal capacities of water at a chosen standard of temperature, which is usually that of the maximum density of water. But since the unit of heat was defined in terms of this same standard, the thermal capacity and specific heat are bound to be numerically equal. Therefore, in order to avoid confusion, in this book specific heat will be taken to be the ratios $\left(\frac{q}{dt} \right)_p$ and $\left(\frac{q}{dt} \right)_v$. The specific heat of a substance is generally a function of the temperature, but in most cases the variation is sufficiently small that the specific heat at a given temperature may be taken as constant and equal to the average specific heat of a neighboring temperature interval of a few hundred degrees.

Detailed consideration of variable specific heats will be given later (page 120).

Inasmuch as the specific heat is a ratio, its numerical value is independent of the system of units employed. Consequently the ratio of Btu per pound per degree F is identical with the ratio of calorie per gram per degree C.

For convenience, the approximate values of the specific heats of a few common substances at ordinary temperatures are given in Table 1-1.

TABLE 1-1 SPECIFIC HEATS OF COMMON SUBSTANCES*

Gases	c_p	c_v
Air	0.24	0.17
Ammonia	0.52	0.40
Carbon dioxide	0.2	0.15
Methane	0.53	0.41
Oxygen	0.22	0.16
Sulphur dioxide	0.15	0.12
Water vapor	0.48	0.36
Liquids †		
Water (for ordinary purposes)	1	
Petroleum	0.51	
Mercury	0.033	
Solids †		
Aluminum	0.21	
Calcium	0.15	
Carbon graphite	0.2	
Copper	0.09	
Iron, cast	0.12	
Lead	0.03	
Silver	0.06	
Zinc	0.09	

From the definition $\left(\frac{q}{dt}\right)$, the specific heat of a substance is the amount of heat required to produce a unit rise in temperature of a unit weight of the substance under specified conditions. Thus, the total quantity of heat added to M units of weight of the substance can be readily

* Compiled from *Handbook of Chemistry and Physics*, 1943, Chemical Rubber Pub. Co.

† Although the small difference between c_p and c_v for liquids and solids is of real theoretical importance to physicists, it is not sufficiently great to be significant in practical engineering processes. Hence, for liquids and solids, c_p is used for specific heat at both constant pressure and constant volume.

determined by knowing the specific heat and measurement of the temperature rise, i.e.

$$Q = Mc(t_2 - t_1)$$

Example

What quantity of heat is required to raise the temperature of 10 lb of air from 50° F to 65° F at constant pressure?

Solution

$$\begin{aligned} M &= 10 \text{ lb} \\ c_p \text{ of air} &= 0.24 \\ t_2 - t_1 &= 65^\circ - 50^\circ = 15^\circ \end{aligned}$$

By direct substitution

$$Q = 10 \times 0.24 \times 15 = 36 \text{ Btu}$$

Latent Heat

When a substance changes from one phase to another, i.e., from solid to liquid or liquid to gas, its temperature remains constant at a value determined by the pressure under which the change takes place. Evidently specific heat has no meaning when applied to such a change, for the temperature does not change with the addition of heat. The amount of heat required to effect the change of phase of a unit weight of a substance is called the *latent heat*. The specific names, latent heat of fusion and latent heat of vaporization, are applied respectively to the change of phase from solid to liquid and from liquid to gas. Values of the latent heat for commonly encountered changes of phase are given in Table 1-2.

TABLE 1-2. LATENT HEATS OF FUSION AND EVAPORATION AT ATMOSPHERIC PRESSURE *

Substance	Latent Heat of Fusion		Latent Heat of Evaporation	
	Gram calories per gram	Btu per pound	Gram calories per gram	Btu per pound
Ammonia	108	194	327	589
Bromine	16	29	44	79
Carbon dioxide	45	81	137	246
Water	80	144	539.5	970
Mercury	2.8	5.0	65	117

* Compiled from *Handbook of Chemistry and Physics*, Chemical Rubber Pub. Co.; *Chemical Engineer's Handbook*, McGraw-Hill; O. W. Eshbach, *Handbook of Engineering Fundamentals*, Wiley.

PROBLEMS

- 1 Outline the field of the science of thermodynamics.
- 2 a. Discuss the Principle of Conservation of Energy
b State the First Law of Thermodynamics and illustrate by some commonplace example.
- 3 a. Outline briefly the general characteristics of the procedure employed by man to transform the energy of natural fuels into useful work
b What is the outstanding influence which limits the efficiency of such transformation?
- 4 Discuss the development of thermometry
- 5 Describe briefly three means of measuring temperature
- 6 Discuss the relationship between centigrade temperature and Fahrenheit temperature.
- 7 a Convert 40°C to degrees F b Convert 220°F to degrees C.
- 8 What is meant by thermodynamic coordinates? How may the state of a substance be specified?
- 9 Define absolute temperature, Btu, absolute pressure, gage pressure.
- 10 a. If the barometric height is 29.2 in. of Hg, change 140 lb per sq in. gage to absolute pressure in lb per sq in.
b Under the same barometric conditions, change 27 in. of Hg vacuum into lb per sq in. absolute.
- 11 If the gage pressure of a certain fluid is 50 lb per sq in. and the barometer is at a height of 29 in. of Hg, what is the absolute pressure? (Mercury weighs 0.491 lb per cu in.)
- 12 a. Convert 25°C to degrees R b. Convert 180°F to degrees K.
- 13 Define energy, heat energy, thermal capacity, specific heat. Discuss fully the meaning of c_p and c_v .
- 14 Translate the symbols $\left(\frac{q}{dt}\right)_p$ and $\left(\frac{q}{dt}\right)_v$ into words and give the names and physical meanings of these relationships.
- 15 Compute the quantity of heat necessary to raise the temperature of (a) 10 lb of petroleum from 60°F to 150°F in Btu, in calories (b) 5 lb of carbon from 30°C to 75°C .
- 16 Considering the specific heat to be constant, compute the heat required to change the temperature of 6 lb of air from 72°F to 120°F (a) when the pressure remains constant, (b) when the volume remains constant.
- 17 Twenty lb of water at 180°F are mixed with 50 lb of water at 70°F . What will the ultimate temperature be?
- 18 A ball of copper weighs 7 lb and is at a temperature of 850°F . It is plunged into a vessel that contains 40 lb of water at a temperature of 60°F . Find the final temperature attained in degrees Rankine. (C of copper is 0.09, of water, 1.0)
- 19 Determine the quantity of heat required to melt 1 cu ft of ice (density 0.92) at atmospheric pressure and the heat required to evaporate the resultant water at the same pressure. Determine the heat necessary to evaporate an equal weight of liquid mercury at the same pressure. Express the answers in both calories and Btu.

Heat and Work

The First Law of Thermodynamics

We have already seen from the introductory discussion and statement of the First Law on pages 1-4 that *heat is a form of energy*. As such, it may be converted into other forms of energy, but the conversion or transformation is always effected in accordance with the Law of Conservation of Energy; i.e., in an isolated system the total amount of energy remains constant. The word "system" in the preceding statement means in a broad sense a region in which there is matter in some form, capable of receiving, storing, and delivering energy. In a restricted sense, any mechanical arrangement for the reception, storage, and delivery of energy is a system. Analytic mechanics supplies many simple examples of this, as for instance a coil spring or a body in the gravitational field of the earth.

Energy is constantly being transformed in a multitude of natural and controlled processes; it will require only a few illustrations to suggest many of them to the reader. One common example of energy transformation is given by the processes attendant upon the operation of an automobile. The heat energy resulting from the combustion of the fuel is obtained by transformation of chemical energy in the gasoline. A part of this heat energy is transformed into mechanical energy by means of the expansion of the gases in the cylinders and drives the car through the mechanism provided for the purpose. The remainder of the heat energy either passes into the atmosphere in the exhaust gases, or is dissipated from the engine by radiation and conduction. It is to be noted that some of the mechanical energy obtained from the heat is used in overcoming friction of the mechanism, but this loss of useful mechanical energy in the form of heat has *nothing to do* with the extent to which heat energy can be transformed into mechanical energy in the particular process under discussion.

The following list indicates a few common processes and devices, together with the energy transformation effected by them.

Process	Transformation
Kinetic friction	Mechanical energy to heat energy
'Generation' of electricity	Mechanical energy to electrical energy
Thermopile	Heat energy to electrical energy
Electric heating	Electrical energy to heat energy
Photoelectric cell	Radiant energy to electrical energy
Electrolysis	Electrical energy to chemical energy
Primary or secondary cell	Chemical energy to electrical energy
Combustion	Chemical energy to heat energy

In this book we shall be concerned principally with transformations involving heat and mechanical energy or work, although some attention will also be given to transformations concerned with heat or work and chemical energy

Exact Meaning of the Word 'Heat'

The word "heat" is loosely used in many connections in everyday language. Until now, the common lack of definiteness in its use has not been serious enough to impair the clarity of the ideas presented. But from this point on, if we are to make any progress at all in thermodynamics, this loose usage must be abandoned and a definite understanding reached once and for all, as to just what heat is and what it is not. Probably it is a holdover from the old and disproved caloric theory of heat that makes us confuse the energy in a heated substance with the energy that put it in that condition. It is easy to make the common and unfortunate error of picturing heat as a weightless fluid that may be either poured into or squeezed from a substance. Actually, *heat is a specific kind of energy in the process of transition*. It is entirely correct to speak of the heat added to or withdrawn from a substance. It is equally wrong to think or speak of the energy *after* its addition or *before* its withdrawal from the substance as being in the form of heat. We are right when we say that the heat *from* a hot water bottle alleviates pain, but we are wrong when we say that the hot water in the bottle has a lot of heat in it. The energy *in* a substance is called *intrinsic energy* and its characteristics are fully discussed in a later paragraph (page 23).

The characteristic property of heat is that its passage from one substance to another is always effected by a temperature difference. If this passage is brought about by molecular interaction when two substances at different temperatures are placed in contact, the process is called conduction. The common experience of burning one's fingers on a hot dish is a vivid and personal experiment in heat transfer by conduction. Whenever heat is transferred by conduction — and this happens

in many problems of engineering thermodynamics — the quantity of heat transferred between two parallel surfaces A square units in cross section and L units apart may be determined by the relation

$$Q = k \frac{A}{L} (t_1 - t_2)$$

where t_1 and t_2 are the temperatures of the two surfaces, and k is a constant which depends on the material separating the surfaces.

A second process of heat transfer is *radiation*. In this phenomenon, the passage of energy from one body to another is effected through the agency of electromagnetic waves set up by vibrations in the atoms of the radiating substance in a certain band of wave lengths. When one stands in front of an open fire he is conscious of the radiant heat energy from the blaze. Again it is correct to designate this energy as heat during the whole time that it is in process of transition, i.e., from the time it leaves the vibrating atoms of the source until it has produced an effect of warmth in the person standing before the fire. But after the effect has been produced, the energy is *no longer* in the form of heat. The evaluation of the quantity of heat transferred by radiation is given by the Stefan-Boltzmann Law as

$$\text{Net radiant energy exchange per unit area} = \sigma(T_1^4 - T_2^4)$$

in which σ is the radiation constant (5.32×10^{-12} watts for ideal black-body radiation), and T_1 and T_2 are the respective absolute temperatures of the radiating and absorbing bodies. Although both bodies are radiating and absorbing heat, there is clearly, in this case as in conduction, a net transfer of energy because of a temperature difference. The quantitative application of the Stefan-Boltzmann Law to engineering problems has hardly begun, but it seems probable that greatly increased attention will be given to it in the future.

Elementary textbooks frequently state that a third process of heat transfer is convection. *This is an error.* The word convection designates the phenomenon by which energy is transferred from one place to another because of the bodily transportation of the matter in which the energy is stored. The movement of air in a house equipped with a hot-air furnace is an excellent example of convection. The energy stored in the warm air is *not* in the form of heat, even though we conventionally say it is.

The essential point of the above discussion is that, in order to keep the analysis straight, the word heat must henceforth always be interpreted as designating energy in the process of transition as a result of a temperature difference.

Definition of Work

In colloquial usage, the word "work" also fails to designate a specific and definite physical concept. However, in the study of analytic mechanics, the student has already learned that from the physical point of view work is related to energy and that work is said to be done when a force acts through a distance. It may be pointed out here that work, like heat, is never used to designate energy that is stored. It is only while mechanical energy is being supplied to or withdrawn from a body, i.e., while a force is acting through a distance, that the energy is in the form of work.

Mechanical Equivalent of Heat

The next consideration in the study of energy transformations must be the establishment of the exact nature of the equivalence of heat and work. Since systems of units are wholly arbitrary, there is no reason to suppose that a unit of heat would be equal to a unit of work. Hence, the question is: Exactly how many units of work represent the quantity of energy equivalent to one unit of heat?

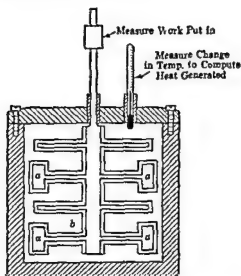


FIG. 2-1 Joule's Paddle Wheel Apparatus
a Revolving arms b Stationary vanes

It was Joule who in the years 1830–1843 first carried out careful and extensive measurements of the relation between mechanical work and the heat resulting from its transformation. His best known apparatus was a water calorimeter in which paddle wheels were rotated in such a way as practically to eliminate all friction except that used in churning

the water (Fig. 2-1). This apparatus made it possible to measure both the mechanical energy, or work, put into the paddle wheels and the resultant heating effect on the water. Later experiments of the same general type performed by others have indicated that the most probable value of the amount of work required to give 1 Btu is 777.64 ft-lb. This constant is called the *mechanical equivalent of heat*. In the cgs system the value of the mechanical equivalent is that 4.18 joules is approximately equivalent to one calorie. The letter J is used to designate the mechanical equivalent. In order to simplify computations, in this book its value will be taken as $J = 778$ ft-lb per Btu.

An understanding of the equivalence of heat and work makes it possible to determine readily the *overall* efficiency of an engine from measurements of the heat energy delivered by the fuel and of the work energy delivered to the shaft.

Example

A certain oil engine burns 0.8 lb of oil per shaft horsepower hour as measured by a brake dynamometer. Determine the overall efficiency if the oil has a heating value of 18,000 Btu per lb.

Solution

$$\begin{aligned}\text{Efficiency} &= \frac{\text{output}}{\text{input}} \\ \text{One horsepower hour} &= 33,000 \times 60 \text{ ft-lb} \\ &= \frac{33,000 \times 60}{778} \text{ Btu} \\ &= 2545 \text{ Btu}\end{aligned}$$

The energy input required for the development of this output is

$$0.8 \times 18,000 = 14,400 \text{ Btu}$$

Therefore, the overall efficiency of the engine is

$$\text{Efficiency} = \frac{2545}{14,400} = 17.67\%$$

Intrinsic Energy

A further consideration, vital to the study of energy transformation, is to determine the amount of energy stored in the system itself at the instant that a thermodynamic change begins and ends. The necessity for this is revealed by the fact that thermodynamics is essentially a matter of bookkeeping that involves energy quantities instead of dollars. As a somewhat naïve analogy, consider the matter of keeping books on one's personal accounts for a month. The first item to be considered is the balance on hand at the first of the month. This, then, is the initial state in which the individual finds himself. Subsequent items

list the amounts received and expended, and the balance on hand at the end of the month indicates the final state of his finances after the change brought about by the month's activities. Clearly, the initial and final balances are essential to any understanding of whatever change has occurred. Similarly, in order to gain any knowledge of what has happened during a thermodynamic change, the energy stored in the system at the beginning and end of the change must be known.

The fact that such energy exists is established by the following considerations. It is common experience that if a closed vessel containing gas under normal conditions is heated, the pressure on the walls of the vessel increases. If the vessel is made in such a way that its own walls do not expand with heating, the volume enclosed remains constant and no effect is produced on the surroundings. The energy of the heat added has gone into the contained volume of gas and its only manifestation is a change in the thermodynamic state of the gas. If now the vessel is connected to a suitable apparatus, say a small turbine, and the gas released, work will be done by the turbine. The gas possessed a store of energy that gave it ability to produce external effects by virtue of the state in which it had been placed. Such energy is called *intrinsic* or *internal energy*, and is denoted by E (e per unit of weight).

Kinetic Theory Explanation of Intrinsic Energy

While thermodynamics is not concerned with the *nature* of intrinsic energy, it is helpful to consider what the kinetic theory of gases has to offer on the subject. According to this theory, which is well supported by experiment, the molecules of a gas above absolute zero are in constant motion. At room temperature many of them have velocities comparable to those of fast rifle bullets. Thus, since each molecule is a discrete mass, it possesses a kinetic energy $\frac{1}{2}mv^2$, where m is taken as mass. There are also attractive forces between the molecules, and although the nature of these forces is more complicated than that given by the Newtonian Law of Attraction Between Masses, they do have the characteristic of varying inversely with some power of the distance, i.e.,

$F = \frac{k}{d^n}$. Consequently a molecule has *potential energy*, depending upon its position with respect to other molecules. The phenomenon of latent heat is an excellent illustration of the potential energy of molecules. We know that when a liquid is vaporized, heat must be added. *The energy represented by this heat is transformed in two ways: one part serves to separate the molecules to the relative positions they occupy under the conditions of the process and so is stored in the medium as potential*

energy; the other part is utilized in doing work on the surroundings to provide for the increase in volume from the change of phase. *The sum of the kinetic and potential energies of molecules* constitutes the energy of the substance and is what is called the intrinsic or internal energy in thermodynamics.

If the volume of gas is constant, the potential energy of the molecules cannot change and so an addition of heat results in increased kinetic energy. Since the addition of heat results in an increase in temperature, it follows that temperature is directly related to the kinetic energy of molecules. Also, since the masses of the molecules are constant, an increase in energy must result in increased velocity of molecules. For a gas that is not highly compressed, the potential energy changes relatively little with change in volume; hence the entire intrinsic energy change of such a medium (potential + kinetic energies of molecules) is virtually dependent only upon the temperature change, i.e., $E = f(t)$. This is entirely consistent with the common observation that, when a gas is compressed, the resulting storage of energy in the medium is manifested by a rise in temperature.

The Conservation of Energy. Bernoulli Equation

The First Law of Thermodynamics is no more than an expression of the Principle of Conservation of Energy. In analytic mechanics this principle, as applied to the energy of a mechanical body, may be expressed in the form

$$\begin{array}{ccccccc} \text{Initial kinetic} & + & \text{moving} & = & \text{final kinetic} & + & \text{resistance} \\ \text{energy} & & \text{work} & & \text{energy} & & \text{work} \end{array}$$

In hydraulics, the Principle of Conservation of Energy is developed into the Bernoulli Equation, which is conventionally expressed as

$$\begin{array}{c} \text{At point 1} \\ \hline \text{Kinetic energy} + \text{pressure energy} + \text{potential energy} + \text{energy supplied} = \\ \hline \text{At point 2} \\ \hline \text{Kinetic energy} + \text{pressure energy} + \text{potential energy} + \text{external work done} + \text{work done against friction} \end{array}$$

In symbols this becomes

$$\frac{u_1^2}{2g} + \frac{p_1}{\rho} + z_1 + \text{head supplied} = \frac{u_2^2}{2g} + \frac{p_2}{\rho} + z_2 + \text{work done} + \text{lost head}$$

In this equation u_1 and u_2 represent the average velocity at points 1 and 2 respectively, g is the acceleration of gravity, p_1 and p_2 denote the pressure at points 1 and 2, ρ is the weight of unit volume of the fluid, and z_1 and z_2 indicate the elevation of the fluid at points 1 and 2 respectively above some arbitrarily chosen datum plane. In order for this equation to be algebraically true, all of its terms must be expressed in consistent units. Conventionally the equation is written in terms of foot-pounds per pound of fluid, which immediately reduces to feet of head. Thus, for one pound of fluid the units for the several terms of the equation are

$$\frac{\left(\frac{\text{ft}}{\text{sec}}\right)^2}{\frac{\text{ft}}{\text{sec}^2}} + \frac{\frac{\text{lb}}{\text{ft}^3}}{\frac{\text{lb}}{\text{ft}^3}} + \text{ft} + \text{ft} = \frac{\left(\frac{\text{ft}}{\text{sec}}\right)^2}{\frac{\text{ft}}{\text{sec}^2}} + \frac{\frac{\text{lb}}{\text{ft}^3}}{\frac{\text{lb}}{\text{ft}^3}} + \text{ft} + \frac{\text{ft} \cdot \text{lb}}{\text{lb}} + \text{ft}$$

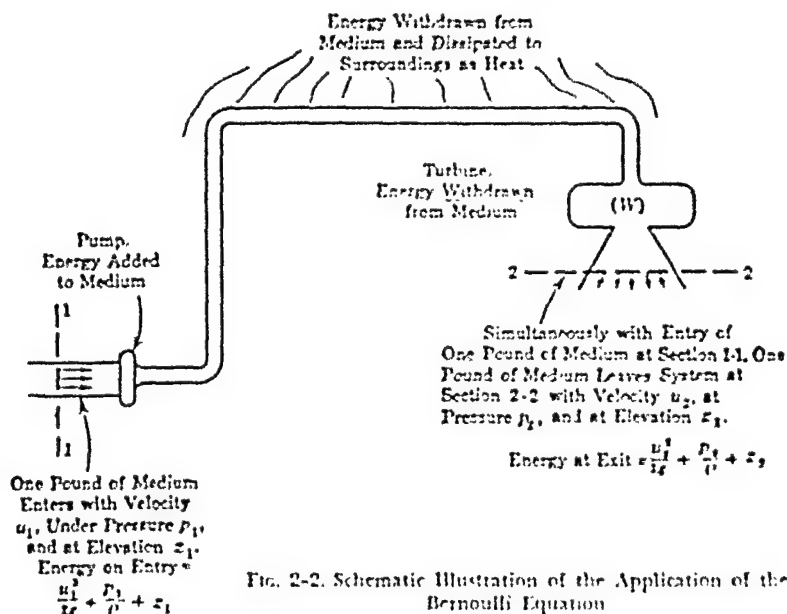
In the application of the Principle of Conservation in both analytic mechanics and hydraulics, the energy supplied or withdrawn from the system is considered as being in the *mechanical* form, i.e., as kinetic or potential energy of the body or mass of fluid as a whole. In the mechanical case, the energy may be supplied or withdrawn as the result of the action of a falling body, the rotation of a shaft, and so forth. External energy supplied a hydraulic system is usually the result of the action of a pump, energy withdrawn from such a system for the purpose of producing an external effect generally acts through the agency of a water wheel or turbine.

Since the Bernoulli Equation is an extension of the elementary expression of the conservation principle of mechanics, it is a special application of the General Energy Equation which, in the broadest sense, includes all possible forms of energy. In view of this, before proceeding to the General Energy Equation, it is worth while to review the conditions under which the Bernoulli Equation is applicable.

Conditions Under Which the Bernoulli Equation Is Applicable

In hydraulics the Bernoulli Equation has to do with the energy possessed either by the same unit weight or by the same M units of weight of the fluid as it passes two separated points in the flow. Fig 2-2 gives a schematic illustration of this application. Evidently the equation is not valid if fluid is either added or withdrawn between the two points, because the equation would not then be dealing with the same continuous stream of fluid. Nor can it be successfully applied if the flow is unsteady, since that would make possible either an increase or a decrease in the quantity of fluid between the two sections. All this is expressed simply

by saying that in the same time during which a unit quantity of fluid enters the system at section 1, an equal quantity must leave at section 2. Hence, in order that the Bernoulli Equation may be applicable, the



flow must be *continuous and steady*. The mathematical expression of continuity of flow is given by the simple and useful Equation of Continuity, i.e.

$$M = \text{const} = \frac{A_1 u_1}{v_1} = \frac{A_2 u_2}{v_2}$$

In this equation M is the weight of fluid flowing in unit time (pounds per second); v_1 and v_2 the specific volume of the fluid (cubic feet per pound) at sections 1 and 2; A_1 and A_2 the area of the stream (square feet) at 1 and 2; and u_1 and u_2 the average velocity of the fluid at 1 and 2.

Steady-Flow Processes

It is a characteristic of many industrial thermodynamic processes for the transformation of energy that they operate steadily and continuously. For example, in a steam plant, water is steadily and continuously pumped into the boiler. Under steady operating conditions, steam formed from this water leaves the boiler and the weight of steam leaving in unit time is the same as the weight of water injected in unit time. If the engine to which the steam is supplied is a reciprocating

ing one, it is true that the steam leaves the engine in puffs of the exhaust and that, strictly speaking, the process is not instantaneously one of steady flow. However, if the flow to and from the engine for a number of revolutions is considered, the process approaches one of steady flow sufficiently to be practically considered so. The same consideration applies to the operation of an internal combustion engine, if the time required for a number of revolutions is considered, the quantity of gasoline and air taken into the engine equals the quantity of the products of the reaction passing through the exhaust. The energy balance principle of the Bernoulli Equation applies to such thermodynamic *steady-flow* processes just as well as it does to the flow of hydraulic fluids.

Non Flow Processes

Although steady flow processes play a dominant role in industrial energy transformation processes, it is nevertheless frequently important to study the energy transformations that take place in a certain definite confined quantity of the medium. Here there is *no flow* of the medium either toward or away from the system. An example of such a process is the expansion of steam in a cylinder for a *single stroke*. The study of the process begins with the steam already in the cylinder and ends when the expansion is completed. *No consideration* is given to the processes by which the steam entered the cylinder or to those by which it leaves. All such processes are called *non flow*, and they are of value in the *detailed* analysis of various engine cycles. Since the Bernoulli Equation applies directly to problems of flow, it is not directly applicable to non-flow processes. It will be shown later (page 36) that the analysis for non flow conditions is readily set up from the fundamental Principle of Conservation of Energy.

General Energy Equation of Thermodynamics

In order to study the steady flow processes of thermodynamics, it will be necessary not only to consider the terms of the Bernoulli Equation, but also to give full consideration to the equivalence of heat and work as expressed by the First Law of Thermodynamics.

First, it must be noted carefully that the Bernoulli Equation of hydraulics (see page 25) is concerned with the energy possessed by the fluid solely because of its inertia and pressure. The weight of fluid considered is in a sense taken as a mechanical body and so its energy is that which it possesses as a whole. But it has been shown above that a thermodynamic medium has intrinsic energy because of the motion and position of its molecules. In hydraulics, since the medium is a

liquid and the temperature change between the two points is usually neglected, the intrinsic energy term does not appear in the equation. The situation is decidedly different in thermodynamics; therefore the first step in the development of the General Energy Equation *must be* the inclusion of the terms e_1 and e_2 , representing the intrinsic energy per unit of weight of the medium at points 1 and 2 respectively.

In a thermodynamic system, consideration must also be given to the possibility of energy supply or withdrawal in the form of heat. Thus, heat energy per unit weight of the medium, designated by q , is incorporated into the equation on the left-hand side. In order that all terms of the equation shall be in the same units, namely foot-pounds, q in heat units must be multiplied by J , the mechanical equivalent of heat.

In addition to the intrinsic energy of a medium resulting from molecular activity, media also possess energy because of their chemical nature. Certainly the energy released by the burning of a pound of oil must have been stored somehow in the hydrocarbons of the oil and the oxygen which made its combustion possible. Both chemistry and physics have clearly established that this energy is stored in the *atomic* structure of the reactants. The combustion of fuel is the *sole and unique process that man has been able to devise for the transformation of the energy resources stored in the materials of the earth*. Consequently no study of thermodynamics is either complete or significant if it does not give importance to the possibility of changes in the chemical energy of the medium. Some authors lump intrinsic energy, dependent upon molecular activity, with chemical energy, dependent upon atomic activity, and call the sum internal energy. In this book, in order to avoid confusion of these two important types of energy, no such grouping of terms is made. Therefore, the General Energy Equation will be extended to include e_1 and e_2 , chemical energy in states 1 and 2 respectively.

A convenient change may be made in writing the term $\frac{p}{\rho}$ for the pressure energy of the medium. The factor $\frac{1}{\rho}$ is the equal of v , the specific volume; i.e.

$$\frac{1}{\text{lb per cu ft}} = \frac{\text{cu ft}}{\text{lb}}$$

In thermodynamic calculations the specific volume is a decidedly more useful term than ρ , the specific weight. Hence in the General Energy Equation $\frac{p}{\rho}$ is replaced by its equal, pv .

The term in the Bernoulli Equation denoting external work done and designated W , remains unchanged, for it is certainly our object

to determine the external effect produced by an energy transformation. So far as thermodynamics is concerned, it is of no importance to segregate external work done into *useful* work and work done against friction of the moving parts of the mechanism involved. Hence the term ${}_1W_2$ refers to the mechanical energy delivered to the mechanism and is the *sum* of the useful mechanical work and the energy dissipated as work done in overcoming mechanical friction.

Electrical energy is another type of energy that should be mentioned. Usually, however, electrical energy in thermodynamic systems may be expressed in terms of either heat or work and so will be treated as such.

With the inclusion of the terms and modifications given above, the Bernoulli Equation for the Conservation of Energy expands to the General Energy Equation, thus

$$\underbrace{\frac{u_1^2}{2g} + p_1 v_1 + z_1}_{\text{Energy of the mass of the medium}} + \underbrace{c_1}_{\text{Internal atomic energy}} + \underbrace{e_1}_{\text{Internal molecular energy}} + \underbrace{J_1 Q_2}_{\text{Heat energy supplied or abstracted}} = \frac{u_2^2}{2g} + p_2 v_2 + z_2 + c_2 + e_2 + \underbrace{{}_1W_2}_{\text{External mechanical work done}}$$

If M pounds of medium are to be considered, each term of the equation is multiplied by M , thus

$$\frac{Mu_1^2}{2g} + p_1 V_1 + Mz_1 + C_1 + E_1 + J_1 Q_2 = \frac{Mu_2^2}{2g} + p_2 V_2 + Mz_2 + C_2 + E_2 + {}_1W_2$$

The capital letters V , C , E , Q , and W signify that the energy quantities to which they refer are possessed by M lb of medium. The subscripts of the terms Q and W signify that they refer to energy in transition between states 1 and 2. In the English system of units, each term of the General Energy Equation as written above is in foot-pounds. Of course the whole equation could be written in terms of heat units by dividing each term by J .

Algebraic Sign Convention for Terms of the General Energy Equation

The term $\frac{Mu^2}{2g}$ refers to kinetic energy possessed by the mass of the medium with respect to a fixed reference system. If the medium is moving at all, it must have a positive amount of kinetic energy and so the sign of $\frac{Mu^2}{2g}$ must always be plus (+).

It has already been pointed out that in thermodynamic calculations absolute pressures are always used. A negative value of absolute pressure is impossible; consequently the sign of the term pV must necessarily always be plus (+).

The quantity Mz refers to the potential energy of the medium above some arbitrary datum plane. If this plane is taken below both point 1 and point 2, the sign of Mz in each case is plus (+). Usually it is more convenient to take the plane at the elevation of the lower of the two points, whence the value of the one is zero and the sign of the other is plus (+).

The terms E and C , the molecular and atomic energy of the medium, are also always plus (+) because each of these forms of energy depends on temperature and the datum of temperature is absolute zero. Just as a negative absolute temperature is inconceivable, so is a negative value for intrinsic or chemical energy.

The sign convention adopted by most students of thermodynamics for Q and W when the General Energy Equation is written in the form given on page 30 is

- + ${}_1Q_2$ indicates heat energy added to the medium during its flow from 1 to 2.
- ${}_1Q_2$ indicates heat energy withdrawn from the medium between 1 and 2.
- + ${}_1W_2$ indicates that external work has been done by the medium on the surroundings between 1 and 2.
- ${}_1W_2$ indicates that work has been done on the medium by the surroundings between 1 and 2.

Since this convention of signs for Q and W is wholly arbitrary, any other convention,* intelligently used, will give equally consistent results.

Enthalpy

The conditions under which many thermodynamic processes operate are frequently such that several of the terms in the Energy Equation are either zero or negligible. In every flow process, however, the terms E and pV have finite values. Intrinsic energy E must have a value because it denotes intrinsic energy above absolute zero. Further, in most processes, the value of E_1 differs from that of E_2 . Pressure energy pV , frequently called flow work, must have a finite value at both sections 1 and 2 in order that the medium may be able to flow past each section. Because these two quantities invariably appear in flow processes, and also since the values for both of them are established by the state of the

* P. J. Kiefe and M. G. Stuart, *Discipline of Thermodynamics*, Wiley, p. 28

medium, it is an advantage to define their sum as a new thermodynamic quantity called *enthalpy*, which is designated by the letter H^* (or h per unit of weight) Thus H , which is always expressed in Btu rather than foot-pounds, is defined by

$$H(\text{Btu}) = E(\text{Btu}) + \frac{pV}{J} (\text{Btu})$$

Values for the enthalpy of steam and other vapors above some arbitrary datum of temperature are tabulated in vapor tables in terms of the coordinates of the state In the case of steam tables, the datum is taken as 32° F Hence, the tabulated values of h give the enthalpy of steam above that state Values for the enthalpy of gases may be directly computed from knowledge of the coordinates of the state, as shown later in Chapter 4

When H is substituted for the sum $E + \frac{pV}{J}$ and multiplied by J so that it is expressed in mechanical units (foot pounds) the General Energy Equation becomes, for M lb of medium

$$\frac{Mu_1^2}{2g} + Mz_1 + C_1 + JH_1 + J_1Q_1 = \frac{Mu_2^2}{2g} + Mz_2 + C_2 + JH_2 + J_2V_2$$

The use of the equation in this form is illustrated by the following examples

Example 1

A boiler operating at a constant pressure of 240 lb per sq in evaporates 4000 lb of water per hour The enthalpy per lb of water injected is 94.7 Btu, and per lb of steam delivered to the main steam line it is 1200.1 Btu Calculate the heat added to the water per hour

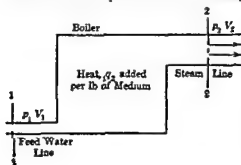


FIG. 2-3

boiler (see Fig. 2-3) The object of the process is to increase the energy of the medium by the addition of heat Clearly the process does not involve any chemical change, and so the terms C_1 and C_2 in the General Energy Equation are equal

Solution

Since the rate of injection of water is the same as that of delivery of steam by the boiler, the process is one of steady flow between a point in the feed line to the boiler and one in the delivery steam line from the

* In the past textbook writers have variously designated the quantity H as total heat, heat content, and total energy Because the connotation of these names is likely to confuse the student, they will not be used in this book they are mentioned here only to facilitate recognition of enthalpy in reference books.

For practical purposes the difference in the potential energy of the medium is negligible in comparison with the other energy quantities involved, and consequently the terms Mz_1 and Mz_2 are taken as equal. Further, in a boiler operating under the pressure stated in the problem, the velocity of injection is not enough different from the velocity of delivery to make a significant difference *

in the kinetic energy terms $\frac{Mu_1^2}{2g}$ and $\frac{Mu_2^2}{2g}$.

Finally, no external mechanical work is done either by or on the medium during the process of evaporation. It is true that a certain amount of energy is involved in providing the space necessary for the medium to enter and leave the boiler, but this is taken care of by the flow-work or pressure-energy terms p_1V_1 and p_2V_2 . The absence of external mechanical effects in the process requires that the term ${}_1W_2$ be zero.

With the simplification brought about by the above considerations, the General Energy Equation for this process reduces as follows:

$$\frac{Mu_1^2}{2g} + Mz_1 + C_1 + JH_1 + J_1Q_2 = \frac{Mu_2^2}{2g} + Mz_2 + C_2 + JH_2 + {}_1W_2$$

$$\text{or} \quad JH_1 + J_1Q_2 = JH_2$$

$$\text{or} \quad {}_1Q_2 = H_2 - H_1$$

Direct substitution of the given values for h_1 and h_2 and for the weight of medium flowing per hour gives the result

$$\begin{aligned} {}_1Q_2 &= 4000(1203.1 - 94.7) \\ &= 4,421,600 \text{ Btu per hr} \end{aligned}$$

With these simplifications, the General Energy Equation for the process is

$$\frac{M u_1^2}{2g} \Big|_0 + M z_1 + C_1 + J H_1 + J_1 Q_1 \Big|_0 = \frac{M u_2^2}{2g} + M z_2 + C_2 + J H_2 + J_2 W_2 \Big|_0$$

or

$$\frac{M u_2^2}{2g} = J H_1 - J H_2$$

Since the velocity attained by the expansion is quite independent of the weight of medium flowing, M is conveniently taken as 1 lb. By direct substitution

$$\frac{u_2^2}{64.4} = 778(1197.8 - 1143)$$

$$u_2 = 1650 \text{ ft per sec}$$

Example 3

Methane (CH_4) is burned in a Bunsen burner with complete combustion at the rate of 0.1 cu ft per min. At atmospheric pressure and 18°C the heat of the reaction



is given as 212,790 calories when the quantities involved are in gram mols and the products have been cooled to 18°C . What is the net difference between the combined intrinsic and chemical energies of the reactants and the products of reaction? Assume that the volume of the condensed water is negligible.

Solution

Steady flow conditions exist in the region where the reaction takes place, i.e., methane and air enter the region at the same rate that carbon dioxide and water vapor leave it. Entrance and exit velocities are both small so that the kinetic energy terms $\frac{M u^2}{2g}$ may be neglected. Likewise, the difference in the potential energy terms ($M z$) is not significant. No external mechanical work is done. Therefore

$$\frac{M u_1^2}{2g} + M z_1 + C_1 + E_1 + p_1 V_1 + J_1 Q_1 = \frac{M u_2^2}{2g} + M z_2 + C_2 + E_2 + p_2 V_2 + J_2 W_2 \Big|_0$$

$$\text{or} \quad (C_2 + E_2) - (C_1 + E_1) = p_1 V_1 - p_2 V_2 + J_1 Q_1$$

From the reaction equation, in each minute 0.1 cu ft of CH_4 combines with 0.2 cu ft of O_2 to yield 0.1 cu ft of CO_2 if the volume of condensed water is neglected. Hence

$$V_1 = 0.1 + 0.2 = 0.3 \text{ cu ft}$$

$$\text{and} \quad V_2 = 0.1 \text{ cu ft}$$

Since 1 cu ft \approx 28.32 liters, V_1 and V_2 in cgs units are

$$V_1 = 0.3 \times 28.32 = 8.496 \text{ liters}$$

$$\text{and} \quad V_2 = 0.1 \times 28.32 = 2.832 \text{ liters}$$

By the terms of the problem $p_1 = p_2 = 1$ atm; therefore

$$p_1 V_1 = 8.496 \text{ liter atm}$$

and

$$p_2 V_2 = 2.832 \text{ liter atm}$$

In thermochemical calculations, equations are conventionally written in units of calories. Hence the equation should be divided throughout by J , bearing in mind that C and E may be expressed in either mechanical or heat units

$$(C_2 + E_2) - (C_1 + E_1) = \frac{1}{J} (p_1 V_1 - p_2 V_2) + {}_1Q_2$$

Or, since in terms of liter atmospheres and calories

$$J = 0.0413 \frac{\text{liter atm}}{\text{cal}}$$

$$(C_2 + E_2) - (C_1 + E_1) = \frac{1}{0.0413} (p_1 V_1 - p_2 V_2) + {}_1Q_2$$

${}_1Q_2$ is the heat of reaction and is given in units of calories per gram-mole. It is therefore necessary to find the amount of CH_4 burned in unit time in units of gram-mole. By Avogadro's Hypothesis, a gram-mole of any gas at atmospheric pressure occupies 23.9 liters at 18°C ; therefore

$$0.1 \text{ cu ft} = \frac{0.1 \times 28.32}{23.9} = 0.1185 \text{ g-mol of methane}$$

We are now ready to substitute the known values in the equation, remembering that ${}_1Q_2$ is negative because it designates heat given off.

$$\begin{aligned} (C_2 + E_2) - (C_1 + E_1) &= \frac{1}{0.0413} (1 \times 8.496 - 1 \times 2.832) + 0.1185 \times (-212,790) \\ &= 24.21(5.664) - 25,216 \\ &= 137 - 25,216 \\ &= -25,079 \text{ cal} \end{aligned}$$

It is to be observed that the decrease in combined chemical and intrinsic energies is actually less than the amount of heat evolved. The volume decrease accompanying the reaction accounts for the difference. Had the volume change been an increase instead of a decrease, the heat evolved would have been less than the decrease in the combined chemical and intrinsic energies by the amount of energy required to produce space for the products of the reaction.

Example 4

Saturated steam at 260 lb per sq in. pressure is supplied to a steam engine which exhausts to the atmosphere. The enthalpy of the entering steam is given in the steam tables as 1201 Btu per lb, and that of the exhaust steam is computed to be 1021 Btu per lb. If 10% of the energy represented by the decrease in enthalpy is dissipated by radiation from the cylinder, how much work is done per pound of steam flowing?

Solution

The difference in the kinetic energy of the entering and the exhaust steam is not sufficiently great in comparison with other terms to warrant consideration

No change in chemical energy is involved. The difference in potential energy terms is negligible. We shall use the form of the General Energy Equation that applies to 1 lb of medium and is in terms of h so that we may substitute the given data directly. Then

$$\begin{aligned}\frac{u_1^2}{2g} + z_1 + c_1 + Jh_1 + J_1q_1 &= \frac{u_2^2}{2g} + z_2 + c_2 + Jh_2 + {}_1W_2 \\ {}_1W_2 &= J(h_1 - h_2) + J_1q_1 \\ &= J(1201 - 1021) + J_1q_1 \\ &= J(180) + J_1q_1 \\ {}_1q_1 &= -0.10(h_1 - h_2) = -0.10(180) = -18 \text{ Btu}\end{aligned}$$

(The sign of ${}_1q_1$ is minus because heat leaves the system.)

$$\begin{aligned}{}_1W_2 &= 778(180) - 778(18) \\ &= 126,036 \text{ ft lb per lb of steam}\end{aligned}$$

Energy Equation for Non-Flow Processes

It is characteristic of a non-flow process that the medium *remains in the apparatus* in which the process takes place. Evidently in such a process the terms of the General Energy Equation that are dependent on the transport of the medium toward and away from the apparatus have no significance. These terms are $\frac{Mu^2}{2g}$, kinetic energy of the medium as a whole, and pV , pressure energy or flow work. Also, the difference in elevation of the center of gravity of the medium before and after a non-flow change is trivial, even in the most exaggerated case. Hence the term Mz may also be neglected. With these changes, the *General Energy Equation for a non-flow process* is

$$C_1 + E_1 + J_1Q_2 = C_2 + E_2 + {}_1W_2$$

This may be readily transposed to become

$$J_1Q_2 = (C_2 - C_1) + (E_2 - E_1) + {}_1W_2$$

The process does not involve any change in chemical energy, hence the equation further reduces to

$$J_1Q_2 = (E_2 - E_1) + {}_1W_2$$

This reduced form is the one frequently found in textbooks. Evidently it is not truly a general equation because with the nomenclature we have chosen it *applies only to non-chemical, non-flow changes of state*. However, most industrial processes involve a succession of different types of state changes, hence for a complete understanding of the whole process, it is not only desirable but frequently necessary to study each of these changes separately. It is for such study that the non-flow equation is particularly useful. The student must keep clearly

in mind the fact that this equation deals with a *single change*, whereas the flow equation applies to a continuously recurring change or *sequence of changes*. The use of the General Energy Equation for a non-flow process is illustrated by the following example.

Example

For the non-flow compression of a certain mass of air 35,000 ft-lb of work are required. During the compression 12 Btu are absorbed by cooling water in the jacket surrounding the cylinder. What is the change in intrinsic energy brought about by the compression?

Solution

Since work is done on the medium by an external agent, the sign of ${}_1W_2$ for this process is minus. The sign of ${}_1Q_2$ is also minus because heat is removed from the medium. Hence, substitution in the equation

$${}_1Q_2 = (E_2 - E_1) + {}_1W_2$$

gives

$$778(-12) = (E_2 - E_1) - 35,000$$

$$778(-12) = \Delta E - 35,000$$

$$\Delta E = +25,664 \text{ ft-lb}$$

Since the sign of ΔE is plus, the change brings about an increase of E of 25,664 ft-lb.

Limiting Types of Thermodynamic Changes

In the most general sense, any thermodynamic medium may change its state in an infinite number of ways. However, for convenience in analysis, such changes may be classified into five elementary types: isothermal, adiabatic, isopiestic (constant pressure), isometric (constant volume), and polytropic. All of these are useful in the study of both flow and non-flow processes.

When the state of a thermodynamic medium changes in such a way that the *temperature always remains constant*, the medium is said to have undergone an *isothermal* change. The expansion of compressed air in its flow along a pipe is an isothermal process. Constant atmospheric temperature is maintained by the influx of heat from the atmosphere through the uninsulated walls of the pipe. It is worth noting that when a medium expands, its temperature generally tends to fall because of the lessening in its store of intrinsic energy. Consequently, if the temperature is to remain constant, energy must be added. Conversely, on compression, when the temperature usually tends to rise, energy must be withdrawn in order to maintain isothermal conditions. Thus, during an isothermal change there is always a transfer of energy which is usually in the form of heat.

An *adiabatic change* is defined as one during which there is *no exchange of energy in the form of heat* between the medium and the external surroundings. Hence, when the General Energy Equation is applied to an adiabatic change, the term ${}_1Q_2$ is zero. The definition implies that the apparatus in which the change takes place is perfectly insulated from the surroundings or that the change occurs so rapidly that there is no appreciable exchange of heat with the surroundings. The definition does not exclude the possibility of heat flow *within* the medium itself as a result of fluid friction or of unequal temperatures at various points in the medium. These are items which will be treated fully in a later chapter. In many actual processes and cycles it is desirable at some stage of the complete process to create conditions that are as nearly perfectly adiabatic as possible. Although the actual realization of the true adiabatic change is probably never achieved, it is approached to a considerable degree in actual machines. The rapid expansion of compressed air in the cylinder of an air engine closely approximates adiabatic conditions in that it takes place so rapidly that there is hardly time for heat to flow in from the surrounding atmosphere.

The definition of an *isoprestic* or constant pressure change is self-evident from its name. Constant pressure processes are particularly adaptable to many industrial uses, as for example, the operation of steam boilers, air-conditioning systems, and industrial chemical processes.

An *isometric* change is defined as one during which the volume remains constant. The experimental determination of heat of combustion in a constant-volume bomb calorimeter is an excellent illustration of a constant-volume process. It should be noted that during a constant-volume change of *any* medium whatsoever no mechanical effect external to the system is produced and hence *no work* is done. Consequently, the term ${}_1W_2$ in the General Energy Equation is always zero for such a change. The constant volume change may be considered as analogous to the mechanical condition in which a force acts but does not produce a displacement. In neither case is any work done.

In actual machines the thermodynamic change that takes place usually cannot be defined by any one of the foregoing types. It has been found, however, that such changes may be closely represented in pV coordinates by the equation $pV^n = \text{const}$. To such changes has been given the name *polytropic*, a word derived from Greek words meaning "many properties." The value of the exponent n in the equation $pV^n = \text{const}$ depends upon the circumstances attending the change in question and must be experimentally determined for that change. Since $pV^n = \text{const}$

applies to *any* state point of the change, it follows that $p_1 V_1^n = p_2 V_2^n$. Hence, substitution in the equation of measured values of p and V for any two state points of the change makes possible the computation of n .^{*} This is accomplished by the ordinary logarithmic method for solving exponential equations. Thus

$$\begin{aligned} p_1 V_1^n &= p_2 V_2^n \\ \log p_1 + n \log V_1 &= \log p_2 + n \log V_2 \\ \text{or } n(\log V_1 - \log V_2) &= \log p_2 - \log p_1 \\ n &= \frac{\log p_2 - \log p_1}{\log V_1 - \log V_2} = \frac{\log \frac{p_2}{p_1}}{\log \frac{V_1}{V_2}} \end{aligned}$$

Point and Path Functions

In the preceding discussion of the several terms of the General Energy Equation it was emphasized that some terms referred to stored energy while others denoted energy in transition. There is an essential difference in the manner of evaluating these two types of terms. It is decidedly worth while to examine the nature of this difference before proceeding to the detailed study of the actual methods of evaluation.

It will be recalled from the elementary calculus that the area under a curve expressed in $X - Y$ coordinates is given by $\int_a^b y \, dx$. In order to evaluate this integral it is necessary to express y in terms of x , i.e., $y = f(x)$. Substitution then makes the integral equal to $\int_a^b f(x) \, dx$, which is readily evaluated. An indefinite number of different kinds of curves might be drawn through the same two end points, each defined by a different function $y = f(x)$. The area under each of these different curves depends on the shape of the curve, and so the area under it may be said to depend on the path that defines it. Since the variables x and y are merely formal symbols in mathematical analysis, the result obtained from the geometric illustration of area may be generalized to apply to the integration of any quantity of the form $f(x) \, dx$. For convenience, all such functions may be called path functions, because the value of their definite integral depends on the path defined by $y = f(x)$. Indeed, unless the equation of the path is known, they cannot be integrated at all.

On the other hand, the student will also recall from the elementary calculus one type of differential expression that *can* be integrated directly, without knowledge of the relationship between the variables. Such an expression is called an exact differential, a simple example of which is $\int_{x_1}^{x_2} (y \, dx + x \, dy)$. The value of the definite integral of an exact differential depends *only* on the values of the function at the two limits and is quite independent of the form of the path between the limits. Thus, for the example given

$$\int_{x_1}^{x_2} (y \, dx + x \, dy) = xy \Big|_{x_1}^{x_2} = x_2 y_2 - x_1 y_1$$

The integral of an exact differential is called a *point function*, examples of it are part of everyone's experience. One commonplace illustration is the fact that the work done against gravity in climbing to the top of a mountain is independent of the path traveled. Consequently, to every point on the earth's surface may be assigned a value representing the work per unit of mass that must be expended against the force of gravity in climbing to that point from some arbitrary datum such as sea level. Thus, gravitational work is a point function. As another illustration of a point function, suppose that the temperature at every point in a room were carefully measured. The temperature distribution in the room would then be identified by the coordinates of the various points. In this case, temperature is a point function, since each point in the room, located by means of rectangular coordinates, has a perfectly definite value of temperature associated with it. It is unlikely that the distribution would be such that it would be easy, or even possible, to determine the *form* of the function, but this difficulty in no way changes its nature as a point function.

Since every point function depends upon the value of the coordinates of a point, a table may be made setting forth the values of the function at suitable intervals in terms of the corresponding coordinates. Such a table could not be made for a *path function*, because knowledge of its values at two different points does not establish the amount of change in the function between those points.

The following illustration will help to distinguish the difference in physical significance, numerical evaluation, and tabulation between point and path functions. Since gravitational work is a point function, the work per unit mass that must be done *against* gravity in reaching various elevations may easily be tabulated in terms of the elevation above a certain datum, usually taken as sea level. But the amount of

a cycle $ABCD$ (Fig 2-5), the medium is restored at the end of the cycle to the state in which it was at the beginning. This means that molecular agitation and configuration, and hence intrinsic energy, are the same after the completion of the cycle as they were before, and illustrates the fact that the value of intrinsic energy depends on the state. It also follows that for a cycle in which the medium returns to its initial state,

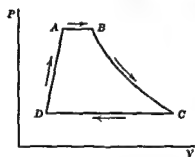


FIG 2-5 Cyclical Process Represented on a PV Diagram

the net intrinsic energy change is zero. Since any two of the three coordinates p , V , and T suffice to fix the state of a medium, we may write

$$E = f(T, V)$$

or
$$E = \phi(p, V)$$

or
$$E = \psi(p, T)$$

Thus it is that with every state point of a medium there is associated a definite* value of intrinsic energy. If a medium undergoes a change from state 1 to

state 2, the change in intrinsic energy ΔE is given simply by $E_2 - E_1$, regardless of the way in which the change takes place. The same principles apply with equal force to the quantities $\frac{Mu^2}{2g}$, Mz , C , and pV .

As enthalpy is the sum of two point functions, $E + \frac{pV}{J}$, it is likewise a point function. Since $\frac{Mu^2}{2g}$ and Mz refer to mechanical energy of the whole mass of the medium, values for them are readily obtained from knowledge of the velocity and elevation respectively. Values for E and H have been tabulated over wide ranges of the coordinates for a considerable number of substances.

Evaluation of ${}_1Q_2$

The quantity of heat added to or withdrawn from a medium may be directly calculated for only two types of change, constant pressure and constant volume. This is because specific heat values have been measured only under these two conditions. Theoretically there is an infinite variety of specific heats, each for a different type of change, but the

* The absolute zero of intrinsic energy has never been established and so the absolute value of intrinsic energy at various state points cannot be written. But this difficulty is of no significance here because we are concerned with the increase or decrease in intrinsic energy resulting from a certain thermodynamic change of state. Just as we choose sea level as an arbitrary datum for measurement of elevation, so may we choose an arbitrary datum of intrinsic energy. Then the simple difference in the values of E above this datum before and after the change of state yields the correct value for intrinsic-energy increase or decrease.

external work is said to have been done by the non-flow expansion of the gas. The amount of work done is $F \times L$, where F is the *total* force acting on the top of the piston and L is the distance the piston moves. Both F and L are readily related to p and ΔV , the change in volume, for

$$p = \frac{F}{A} \quad \text{and} \quad \Delta V = LA$$

where A is the area of the piston face. Then

$$p \Delta V = \frac{F}{A} \times LA = FL = \text{work done against the piston}$$

If the change in volume is taken smaller and smaller, the work done becomes smaller in the same measure and so in the limit of $dW = pdV$. The necessity of going to the differential form of the expression becomes immediately apparent when we realize that in this illustration the pressure remained constant. Usually the expansion of a gas results in a continuous drop in pressure directly related to the change in volume. Therefore, in order to evaluate work as $p \Delta V$, we must take a change in volume so small that the pressure remains practically constant during the infinitesimal change. The total work for the entire change will

then be given by the definite integral of $p dV$ between the limiting conditions

$$W_2 = \int_{V_1}^{V_2} p dV$$

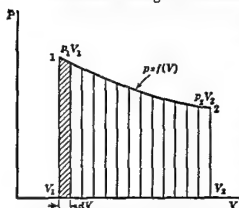


FIG 2-7 Path of Expansion and Work of Expansion Represented on a pV Diagram

As an example it will be helpful to consider the graphic representation of the expansion of a medium and the work done by it. In Fig 2-7 the curve 1-2 represents on the pV diagram the continuous change of state of a medium as it expands from state 1 to state 2.

(p_1V_1 to p_2V_2) Evidently the pressure is constant only for the infinitesimal change of volume dV . Since $dW = pdV$, the work done during this infinitesimal change of volume is represented by the shaded area pdV . The process of integrating the differential expression to obtain the total work done involves no more than the addition of all the strips pdV from V_1 to V_2 . It therefore follows that the *work done by an expanding medium in a non flow process is represented by the area under the curve on the pV diagram that represents its change of state*. Gases and vapors can change their state in a vari-

Hence, for convenience, the value of $p_2 V_2^n$ is taken for evaluating the first term of the numerator of (1), and $p_1 V_1^n$ for the second. Then

$${}_1W_2 = \frac{p_2 V_2^n V_2^{-n+1} - p_1 V_1^n V_1^{-n+1}}{-n+1} = \frac{p_2 V_2 - p_1 V_1}{1-n}$$

It is to be noted that this equation is valid for any value of n except $n = 1$, in which case the expression for ${}_1W_2$ becomes indeterminate. Since the change represented by $n = 1$ is important, further attention must be given to the value of ${}_1W_2$ for it. If the initial analysis is repeated for the case $n = 1$, there results

$$pV = \text{const} \qquad p = \frac{\text{const}}{V}$$

$$\text{and} \qquad {}_1W_2 = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{\text{const}}{V} dV = \text{const} \int_{V_1}^{V_2} \frac{dV}{V}$$

The student will recall from the elementary integral calculus that the evaluation of this integral differs from that of the general case $\int \frac{dV}{V^n}$ and is, in fact, given by the natural logarithm of the variable. Thus

$$\begin{aligned} {}_1W_2 &= \text{const} \left[\int_{V_1}^{V_2} \frac{dV}{V} = (\text{const}) \log_e V \right]_{V_1}^{V_2} \\ &= \text{const} \log_e \frac{V_2}{V_1} \end{aligned}$$

The value of the constant is given by the measured values of p and V for any state point of the change, i.e.

$$p_1 V_1 = p_2 V_2 =$$

Therefore, when $n = 1$ in $pV^n = \text{const}$

$${}_1W_2 = p_1 V_1 \log_e \frac{V_2}{V_1} \quad \text{or} \quad p_2 V_2 \log_e \frac{V_2}{V_1}$$

Since $p_1 V_1 = p_2 V_2$, this equation may be expressed in terms of p by the following substitution

$$p_1 V_1 = p_2 V_2, \quad \frac{p_1}{p_2} = \frac{V_2}{V_1}$$

Substituting gives

$${}_1W_2 = p_1 V_1 \log_e \frac{p_1}{p_2} \quad \text{or} \quad p_2 V_2 \log_e \frac{p_1}{p_2}$$

The use of the above equations for the evaluation of the work function ${}_1W_2$ is illustrated in the following examples

The work of compression per stroke is now obtained from

$${}_1W_2 = \frac{p_2V_2 - p_1V_1}{1 - n} = \frac{80 \times 144 \times 1.25 - 14.5 \times 144 \times 4.7}{1 - 1.29}$$

$${}_1W_2 = \frac{14,400 - 9810}{-0.29} = -15,800 \text{ ft lb}$$

By convention, when the sign of ${}_1W_2$ is minus, it is taken to mean that work is done *on* the system by the surroundings. This, of course, is the case in compression (see page 31)

Work Done in Cyclical Processes

The use of the graphic representation of ${}_1W_2$ is decidedly helpful when it is desired to determine the net work done in a series of changes such as are encountered in any cyclical process. Fig. 2-8 shows a cyclical process in terms of pV coordinates. The change AB is an expansion

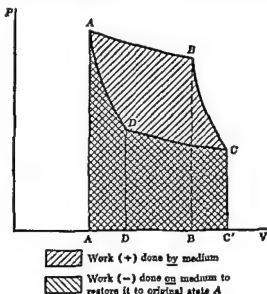
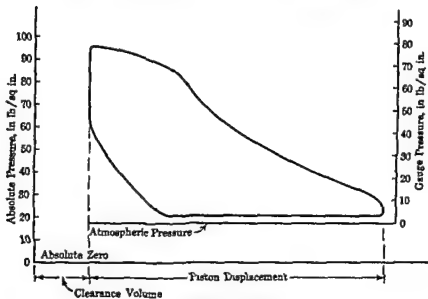
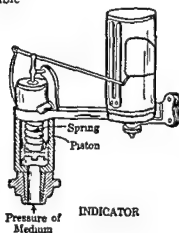


FIG. 2-8 Net Work of a Cyclical Process

Hence it represents work done *by* the medium which by the sign convention we have adopted is given the algebraic sign of plus. The change BC is likewise an expansion and the work done by it is also plus. The changes CD and DA , however, are compressions, that is, work is done *on* the medium by the surroundings and the integrals of $p dV$ for these changes are *inherently negative*.

* Note the conversion of pressure to pounds per square foot in order that work may be expressed in the conventional units of foot pounds.

- 7 It is claimed that a certain heat engine delivers 300,000 ft-lb of work per hour and during this period receives 350 Btu of heat. Are such results possible?



INDICATOR CARD

FIG 2-9

(Reprinted from *Elements of Heat Power Engineering Part I* by Barnard Ellenwood and Hirschfeld published by John Wiley & Sons Inc.)

- 8 Discuss steady flow process, non flow process
- 9 State the forms in which stored energy may exist. What name and symbol are used to signify jointly the kinetic and potential energy stored in the molecules of a thermodynamic substance? How is atomic energy specified in the General Energy Equation?

- 24 Discuss the meaning of the terms thermodynamic system, thermodynamic process, thermodynamic cycle. Illustrate.
- 25 If the intrinsic energy of a thermodynamic medium is in mechanical form, how is it that an adiabatic change results in a change in temperature?
- 26 During the compression of 1 lb of air in a non flow process 10 Btu are removed by the cooling water and 30,000 ft lb of work are required. What is the change in intrinsic energy of the air? If the initial temperature of the air was 80° F and $c_v = 0.23$, what is the final temperature?
- 27 How may energy which is transformed into work by means of a thermodynamic change be evaluated? In what units will it ordinarily be expressed?
- 28 During a non flow adiabatic change of state of a medium, 15,000 ft lb of external work are done. What is the change in intrinsic energy of the medium? In foot pounds? In Btu? Will the temperature of the medium rise or fall as a result of the change?
- 29 The change in enthalpy per pound for air compressed adiabatically from an initial absolute pressure p_1 and volume v_1 to final absolute pressure p_2 and volume v_2 is given by the expression

$$\frac{1}{J} \frac{k}{k-1} (p_2 v_2 - p_1 v_1)$$

Derive an expression for the change in e for the compression.

Note k is the value of n in $pV^n = \text{const}$ for adiabatic change of a gas. The expression for e will be derived in a different analysis in the chapter on ideal gases.

- 30 Using the expression in Problem 29, determine the mechanical efficiency of a compressor unit which requires 51,000 ft lb to compress adiabatically 1 lb of air from 14.4 lb per sq in. abs and 10.45 cu ft to a pressure of 136.7 lb per sq in. abs and a volume of 2.09 cu ft. Use $k = 1.4$.
- 31 In a non flow process a medium undergoes a change of state from an initial volume of 10 cu ft and pressure of 150 lb per sq in. abs to a final volume of 25 cu ft and pressure of 60 lb per sq in. abs. The equation of the path is $pV = \text{const}$. Compute the external work done. Is this done on or by the medium?
- 32 A non flow change of state of a medium occurs at a constant volume of 10 cu ft. The pressure increases from 20 lb per sq in. abs to 100 lb per sq in. abs. Is any external work done? Does intrinsic energy increase or decrease? Must energy be added or abstracted? What relationship must exist between the energy added or abstracted and the intrinsic energy change?
- 33 In a non flow process a medium undergoes a change of volume from 50 cu ft to 25 cu ft at a constant pressure of 100 lb per sq in. abs. What is the equation of the curve representing the path on the pV plane? Is work done on or by the medium? How many foot pounds? If 200 Btu of energy leave the medium in the form of heat during the process, what is the change in intrinsic energy?
- 34 A medium having an initial volume of 10 cu ft and pressure of 150 lb per sq in. abs undergoes a non flow change of state to a final volume of 25 cu ft and a pressure of 49.4 lb per sq in. abs. The equation of the curve on the pV diagram representing the change is $pV^{1.2} = \text{const}$. Compute the external work done. Is this work done on or by the medium?

potential energy as that with which it started. The upswing was therefore an ideal reverse process to the downswing, because the pendulum returned to its initial state and the entire amount of energy transformed was ultimately completely restored to its initial form.

Another example of reversibility is given by a frictionless adiabatic change of state. Imagine that a bicycle pump has its outlet sealed off. In order to insure the adiabatic property, conceive the pump barrel to be so perfectly insulated that no heat can enter or leave from the surroundings. Now suppose the plunger to be pushed down so slowly that no turbulence or internal friction occurs, and let the amount of work done be carefully measured. If, after compression, the pump handle is released as slowly as it was pushed down, just as much work will be obtained from the expanding gas as was expended in compressing it and finally the medium will return to its exact original state. Evidently, if absolutely all internal friction and turbulence are to be avoided, the process will have to be carried out infinitely slowly, a procedure which is clearly impossible.

From the foregoing examples, the student might get the idea that it is the absence of friction which is the essential feature of a reversible process. *Such a conclusion is inadequate.* All natural processes that involve energy in the form of heat are inherently irreversible. Because heat flow naturally occurs *only* from a region of higher temperature to one of lower temperature, heat flow in the reverse direction can be accomplished only by the supply of additional energy from an outside source. We can, however, conceive an ideal limiting process in which reversible heat flow occurs. To do so, we must consider that the heat flow occurs isothermally. This violates the natural law that heat flows only from a higher to a lower temperature. But if we imagine the temperature difference to be infinitely small, we revert to the idea of a reversible process being one in continuous equilibrium in which an infinitesimal change of coordinate (in this instance temperature) will reverse the direction of the process.

The usefulness of the idea of a reversible process lies in the fact that it defines an ideal from which the deviation of practical processes may be measured. It is by means of quantitative knowledge of the amount of this deviation or degree of irreversibility that the efficiencies of similar processes may be intelligently compared. Furthermore, the same knowledge is invaluable in pointing the way toward the possibility of improving processes and cycles so that they may more nearly approach the ideal.

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Initially, consider that the medium in the cylinder is at an elevated temperature T_1 , and that the piston is at position 1. The cylinder is then placed in contact with a body also at T_1 and so large that the withdrawal of heat from it does not lower its temperature. Such a body is called an *infinite source* of heat. The external pressure on the piston is assumed to be maintained infinitesimally less than that of the medium and so the latter expands. When any medium expands, the temperature tends to fall because intrinsic energy, which has already been shown to depend on temperature, is the immediate source of energy for the work of the expansion. Of course, in many processes, as in this one, the store of intrinsic energy is immediately replenished from another source. In the present case, as soon as an infinitesimal quantity of work has been done, the temperature falls infinitesimally and an infinitesimal quantity of heat flows in. The addition of this heat to the medium restores its temperature to the initial value T_1 . Then another infinitesimal amount of work is done, again the temperature falls infinitesimally, and again heat flows in from the source. The expansion continues in this fashion, with the temperature at any point in the medium never departing more than infinitesimally from T_1 , until the piston reaches point 2 (Fig 3-1a). It was assumed at the outset that all the processes of the cycle were reversible. Hence, in the limit, as the infinitesimal changes in temperature approach zero, the change of state accompanying the displacement of the piston from 1 to 2 is a *reversible isothermal expansion*.

For the second process of the cycle, the cylinder is considered to have been removed from the infinite source of heat and placed on a block of perfect insulating material. Since the cylinder walls and piston are similarly insulated, *no heat can enter or leave the medium*. The medium, however, continues to expand *adiabatically and reversibly* until the piston reaches point 3. During this expansion the work done by the medium on the piston is wholly at the expense of intrinsic energy, for there is no other possible source of energy. Consequently, the temperature of the medium falls decidedly during the process. Let its temperature at the end of the expansion be T_2 , which is of course less than T_1 .

In order to complete the cycle, the medium must be restored to its initial state point 1. This might be done by retracing the paths of the two expansions by adiabatic and then isothermal compression. However, if this were done, the amount of work done *on* the medium in compression would be exactly equal and opposite in sense to that done *by* the medium on expansion. Thus no net useful effect would be derived from the cycle. Since the object of the cycle is to derive the maximum useful effect, the medium must be returned to its initial condition over a

path different from that over which it expanded. This is achieved by first compressing the medium isothermally and then compressing it adiabatically. We shall assume that the external work done during the isothermal and adiabatic *expansion* was used to store energy in an external system. It will be necessary to withdraw *some* of this energy to effect the compressions. The remainder then constitutes the net work of the cycle.

For isothermal compression the cylinder is considered to be placed in contact with a body also at T_2 and variously called the cold body, receiver, condenser, or refrigerator. It is assumed that this body is so large that the addition of heat to it does not alter its temperature; hence it is called an *infinite refrigerator*. A force F is then applied to the piston, so that the pressure on the medium is maintained infinitesimally greater than its own pressure. The piston moves downward, and an infinitesimal quantity of work is done on the medium. This tends to raise its store of intrinsic energy and hence its temperature. The infinitesimal temperature difference, however, makes possible the flow of an infinitesimal quantity of heat to the refrigerator. This sequence of infinitesimal energy changes, which is the reverse of those that took place on the isothermal expansion 1-2, is continued until the piston reaches point 4.

For the final process of the cycle, the cylinder is again considered to be placed on the insulating block. The application of external force to the piston is continued, with the magnitude of the force increasing in such a way that the pressure on the medium is never more than infinitesimally greater than the pressure of the medium itself. Because of this and because no heat flows, the process is a *reversible adiabatic compression*. All of the work done on the medium through the action of the external force is therefore stored as intrinsic energy. Consequently, the temperature *rises*, and the compression is continued until the temperature T_1 , as well as the pressure and volume of the initial state point, has been achieved. This occurs when the piston has reached point 1 in Fig. 3-1d. The cycle of operations is therefore completed at this point.

The Non-Flow Energy Equation applies directly to the several processes of the Carnot cycle, since they are all non-chemical, non-flow changes of state. It is decidedly helpful in the analysis of the whole cycle to write this equation for each change of the cycle, thus

$$\text{Isothermal expansion 1-2} \qquad {}_1Q_2 = \frac{1}{J} [(E_2 - E_1) + {}_1W_2]$$

$$\text{Adiabatic expansion 2-3} \qquad 0 = \frac{1}{J} [(E_3 - E_2) + {}_2W_3]$$

operate as a heat pump. That is, upon supplying mechanical energy to it, it will take in heat at a low temperature, add to it the heat equivalent of the work done on it, and finally reject the sum of these two quantities of heat at the high temperature. A numerical example will help

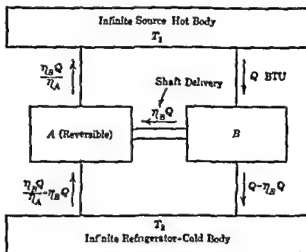


FIG 3-3

to make this clear. Suppose that cycle A has an efficiency of $\eta_A = 0.4$. This means that when operated as a motor, 0.4 Btu of mechanical work is done for 1 Btu supplied at the high temperature and 0.6 Btu is rejected to the refrigerator. When operated on the reverse cycle as a heat pump, for every 0.4 Btu supplied as mechanical work, 0.6 Btu is absorbed from the cold body and added to the 0.4 Btu supplied as work, and finally 1 Btu is rejected to the hot body. Hence, for the reversed cycle, the work done on the shaft, multiplied by the reciprocal of the motor efficiency, gives the heat rejected to the hot body. To return to Fig 3-3, if cycle B supplies $\eta_B Q$ Btu of energy in mechanical form to the shaft driving cycle A , there will be returned to the source $\frac{1}{\eta_A}(\eta_B Q)$ heat units. If

the ratio of η_B to η_A is greater than 1, a greater quantity of heat will be rejected to the hot body than was taken from it. This would mean that in the entire system made up of the source, cycles A and B , and the refrigerator, heat was flowing from a low temperature to a higher temperature without expenditure of work. But this is impossible because of the Second Law of Thermodynamics. Therefore η_B cannot be greater than η_A and the conclusion is that no cycle can have a greater efficiency than a reversible one. The Carnot cycle, which is a reversible cycle, satisfies the first criterion for maximum efficiency.

5-6 in Fig 3-4. Hence the amount of heat Q_2 rejected to the refrigerator is greater than is the case when the isothermal compression is uninterrupted. This further increases the value of the fraction $\frac{Q_2}{Q_1}$ in the efficiency equation, and *further* decreases the value of the efficiency of the cycle. Of course, the change of temperature during the addition or withdrawal of heat might come about in many different ways from the one described. In every case, however, the effect of such changes of temperature may be analyzed in this fashion. The result of all these analyses invariably leads to the conclusion that even in a reversible cycle maximum transformation of heat into work occurs only when heat is both *added to and withdrawn from the cycle isothermally*. Thus it is that in the ideal Carnot cycle heat is added during an isothermal expansion and withdrawn during an isothermal compression.

Thermodynamic Scale of Absolute Temperature

The third item of the Carnot Principle involves consideration of the scale upon which temperatures T_1 and T_2 are to be measured. On page 6 it was shown that a unit of temperature is expressed in terms of the expansion of some thermometric substance between arbitrarily selected points. In the foregoing discussion of the Carnot cycle it was stated that the heat must be supplied to the working fluid at the highest possible constant temperature, and the working fluid must reject heat at the lowest possible constant temperature. Nothing was said as to what values these temperatures should have. They were simply taken to indicate relative degrees of hotness without regard to any temperature scale or method of measurement. From this it appears that the Carnot cycle may be used to define a temperature scale which will be absolute in the sense that it is quite independent of the nature of any thermometric substance.

Suppose that a series of Carnot cycles is devised, with the refrigerator of one cycle constituting the source of heat for the cycle following it (Fig 3-5). If this sequence of cycles is indefinitely continued, a point will eventually be reached where, in the last cycle, all of the heat added is converted to work and there is no heat to be rejected. At this point, then, the temperature T_2 must be absolute zero. Now if these cycles are devised in such a way that the temperatures of addition and abstraction of heat are at *equal intervals*, it becomes possible to define an absolute temperature scale. When this is done, it turns out that there is no significant difference between the absolute thermodynamic scale defined by the Carnot cycle and the absolute temperature scale as given by a

gas thermometer. Also, the quantities of heat added and withdrawn from the several individual cycles are proportional to the defined absolute temperature.* Consequently, Q_1 is proportional to T_1 , the

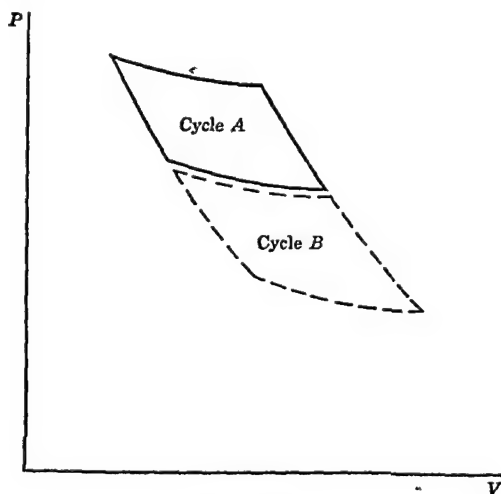


FIG. 3-5.

higher absolute temperature, and Q_2 to T_2 , the lower absolute temperature. Therefore the third criterion for maximum transformation of heat into work is expressed by using this proportionality to write the equation for Carnot efficiency in terms of absolute temperatures, thus

$$\eta_{\text{Carnot}} = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

It will be found that the expression

$$\eta_{\text{Carnot}} = \frac{T_1 - T_2}{T_1}$$

is decidedly more useful in problems involving Carnot efficiency than the expression in terms of Q , for the temperature of rejection is more easily measured than the heat quantity rejected. *It must be understood that this expression is not valid for determining the actual efficiency of practical cycles.* The latter efficiency approaches Carnot efficiency only in the measure that the conditions under which these cycles operate approach those of the Carnot cycle. The determination of Carnot efficiency is illustrated by the following example.

* G. A. Goodenough, *Principles of Thermodynamics*, Holt, 3rd ed., p. 58.

Example

A heat cycle operates between temperatures of 420° F and 60° F. If 3000 Btu are supplied this cycle, what is the maximum amount of work that can be obtained from this heat?

Solution

$$\begin{aligned}\eta_c &= \frac{T_1 - T_2}{T_1} \\ &= \frac{(420 + 460) - (60 + 460)}{420 + 460} \\ &= 41\% \text{ approx}\end{aligned}$$

$$3000 \times 0.41 = 1230 \text{ Btu maximum heat converted to work}^*$$

$$1230 \times 778 = 957,000 \text{ ft lb approx}$$

Factors Affecting Carnot Efficiency

Inspection of the factors of the efficiency equation shows that Carnot efficiency can be improved by increasing the temperature of addition, T_1 , or decreasing the temperature of rejection, T_2 . Both of these ideas have been and are continually being applied industrially in order that greater mechanical effect may be obtained from heat. For example, in modern steam engine practice, higher and higher pressures with correspondingly higher temperatures are constantly being employed. Likewise, the steam engineer makes every effort to have the steam exhaust to a condenser at the lowest possible pressure, with correspondingly low temperature. The same trend is evident in modern designs of internal combustion engines. In the last few years, compression ratios in automobile engines have been greatly increased. This change of design results in increasing the temperature of combustion, with consequent possibility of gain in efficiency. Whether this possibility is realized depends on the mechanical features of the engine as well as upon the chemical and physical properties of the fuel.

It is of vital importance for the engineer to appreciate the strict Carnot limitation upon the efficiency of transformation of heat energy to mechanical energy, because from time to time he will be called on to pass upon the validity of schemes that aim to circumvent it.

Example

An inventor claims that a certain engine has a fuel consumption of 0.3 lb of oil per brake hp-hr developed. The highest temperature obtained in the engine is 2500° F and the engine exhausts at 800° F. The oil has a heating value of 12,000 Btu per lb. One brake hp-hr is equivalent to 2545 Btu. Are the inventor's claims possible?

* This is the maximum heat which could be converted to work by a Carnot cycle operating between the given temperatures.

Solution

$$\begin{aligned}\text{Carnot efficiency} &= \frac{T_1 - T_2}{T_1} \\ &= \frac{(2500 + 460) - (800 + 460)}{2500 + 460} \\ &= 57.3\%\end{aligned}$$

Claimed efficiency:

$$\frac{\text{Output}}{\text{Input}} = \frac{2545}{0.3 \times 12,000} = 71\%$$

Whether he is doing it willfully or not, the inventor is deluding himself.

The Second Law of Thermodynamics

An initial assumption to all that has been said about the Carnot cycle and principle was that heat was to be added at a relatively high temperature and rejected at a relatively low one. There is nothing in the First Law to require that this be done. This law states only the equivalence of various forms of energy, but gives no information as to the direction a given transformation should take. The First Law takes no exception to the possibility of having a cycle in which heat is wholly transformed into work. *Experience has invariably shown that this never happens.* The question then is: What are the limitations on the transformation of heat into work? The answer is embodied in the principle known as the Second Law of Thermodynamics, which is every bit as fundamental as the First Law.

A great many eminent scientists have made statements of the Second Law. Probably the simplest of these is the one by Clausius, already given in Chapter 1 (page 4). This statement may be paraphrased by saying that *heat cannot of itself, i.e., without compensation, pass from a cold to a hot body.* This means that heat has the unique property, inherent in its nature, of flowing naturally only in *one* direction, from hot to cold. Consequently, heat cycles are devised so that the temperature of the medium is lowered by the removal of energy in the form of work, thus making it possible to reject energy in the form of heat at a temperature lower than its temperature of supply. If any heat is to be transformed into work, the flow *must not be* direct, as in conduction, because in that case *all* of the heat that flows enters the colder body and there is no energy left to be transformed into work. The process must be one in which the medium absorbs heat at the higher temperature, undergoes alternate expansions and compressions as the result of which work is delivered to the surroundings, rejects a part of the heat at a lower temperature, and is ultimately restored to its initial state. Ideally, the *difference* between the

heat added and that rejected is transformed into work. Such a cycle is in accord with the Second Law because heat does pass from hot to cold.

The phrase "without compensation" in Clausius' statement is of considerable importance and merits further consideration. In any refrigerating cycle, which is in fact only a reversed heat engine, the cooled substance is kept at a low temperature by withdrawing heat from it. This heat is subsequently rejected to the surroundings at a higher temperature. But the slightest acquaintance with a household electric refrigerator or even with the bills for its power consumption is enough to impress on anyone that this flow of heat from cold to hot is accomplished *only by the expenditure of work*. If it were possible to make heat flow from cold to hot without compensation, i.e., without the expenditure of work, it would be possible to collect the vast quantities of low-temperature heat in the earth, the seas, and the atmosphere, raise it to a high temperature, and use it as a source of energy for heat engines. A scheme of this sort would achieve a kind of perpetual motion, which, because its existence is denied by the Second Law, is called perpetual motion of the second kind.

In the light of this analysis, another statement of the Second Law given by Planck takes on considerable significance. His statement is as follows: "It is impossible to construct an engine which will work in a complete cycle, and produce no effect other than the raising of a weight and the cooling of a heat reservoir." The reason for the stated impossibility of building such an engine is that it does not provide for a lower temperature to which the heat can flow. If such an engine were possible, it also would achieve perpetual motion of the second kind, because Planck specifies no particular temperature for the heat reservoir. He says simply that it is impossible to transform a quantity of heat wholly into an equivalent quantity of mechanical work. This denies the possibility of using low temperature heat as an energy source just as effectively as does the statement of Clausius. By Planck's statement low-temperature heat can be used as an energy source *only* when a yet lower naturally occurring temperature is available to which the heat can flow. Since the temperature of the earth, the seas, and the atmosphere is always, at a given place, the lowest naturally occurring temperature, no heat can flow from these sources and hence no energy transformation into work can occur.

The essential point about the Second Law is that it is concerned with the peculiar properties of heat, whereas the First Law deals with the equivalence of all forms of energy. Thus it is that the Second Law has no counterpart in mechanics but is encountered for the first time in

thermodynamics. It is of *fundamental* importance because heat is the ultimate source of energy for *every known process* for the development of mechanical power. Moreover, not only is it true that heat *can* pass from a higher temperature to a lower; everyday experience shows us that it *does* so at every opportunity. And once it reaches the natural temperature of the surroundings, all possibility of transforming any part of it into work is forever gone. It has become a degraded sort of energy which, whether we like it or not, must be considered as having been thrown on the waste heap of the universe.

There is only one way in which the engineer can even partially circumvent this constant degradation of heat energy. *He can and should take every measure possible to insure that whenever heat flows it does so only in the most efficient cycle for its transformation into work that is possible under the circumstances.* When this is not done, there is an irretrievable waste, not of energy but of transformable energy. An extreme example of this waste is given by the ordinary hot-air furnace, commonly used for heating houses. In the firebox of such a furnace, the heat of combustion of the fuel raises the temperature of the gases to about 2500°F . But the householder certainly has no use for them at that temperature! He simply wants his house to be comfortably warm at about 70°F . The energy is therefore permitted to slide down the temperature gradient without the transformation of any part of it into work. Not only that, but once at 70°F , the possibility of *ever* being able to transform any part of that particular quantity of heat is gone. As long ago as the middle of the last century Lord Kelvin clearly saw the enormous wastefulness of this process and suggested that houses might be much more efficiently heated by a modified reversed Carnot cycle. No practical application of his idea was made until a few years ago, when an extensive research investigation of the idea was begun at the Mellon Institute in Pittsburgh. It is well within the realm of possibility that the results of this research may lead to a change in the methods of house heating no less revolutionary than the change in transportation methods brought about by the development of the automobile.

Entropy

In the discussion of the Carnot cycle it was found to be a decided convenience and help to study the work done during the several changes in terms of the areas under the curves on the pV diagram. In order to establish clearly the amount of heat that is transformed into work in any particular process or cycle, it is evident that it would be similarly helpful to be able to represent heat quantities in terms of area on some

coordinate system. The graphic representation of work depends on the fact that the dimensions of work are easily identified with the elementary coordinates p and V . But the definition of unit heat quantity (Btu or calorie) involves only *one* elementary coordinate, temperature. Therefore, if heat is to be represented graphically as an area, another quantity must be determined of such nature that its product with temperature has the dimensions of heat. The need for such a quantity was clearly seen early in the history of thermodynamics, and to supply that need a coordinate called entropy was arbitrarily defined, or invented. Entropy of heat energy, designated by S , is defined as the quotient of heat quantity divided by the absolute temperature. On the basis of the simplest kind of arithmetic, the product of entropy multiplied by absolute temperature must be heat quantity. The definition therefore gives the single and unique quantity that satisfies the requirement of being the second factor of heat. There are a number of important physical quantities that are the product of two factors, one of which may be called intensive, the other extensive. The intensive factor denotes the *intensity* of the quantity acting, the extensive factor gives the *extent* to which it acts. Thus, mechanical work is the product of force times distance, in which force is the intensive factor, and distance the extensive factor. In the product for the work done by an expanding medium, i.e., $\int p dV$, pressure is the intensive factor, and the change in volume the extensive factor. In electricity, it is shown that work is equal to electromotive force times quantity of electricity. Here electromotive force is the intensive factor, and electrical quantity the extensive factor. From these illustrations it becomes clear that temperature has the nature of an intensive factor. Since the product of temperature and entropy gives heat, it follows that entropy may be defined as the extensive factor of heat energy. Of course, in a sense, entropy differs from the extensive factors cited as examples in that it is an arbitrary invented quantity and not a physical one. It is abstract, not concrete. In no way, however, does this disability impair its great usefulness in the consideration and solution of problems concerned with heat energy.

The subject of entropy has long been a source of difficulty for the beginning student in thermodynamics. The difficulty has arisen because somewhere in every discussion of the subject there must come a shift in the point of view with which entropy is regarded. Unless this shift is clearly pointed out, the student is apt to miss it and from that moment subsequent discussion only confuses him more and more. In order to avoid this difficulty, we propose to point out definitely what the shift is and why it is necessary. In the preceding paragraph entropy was defined

as the extensive factor of heat energy. As the student learns this definition he must keep clearly in mind that heat is always energy in transition. Consequently, he must not think of a quantity of heat as a static chunk of energy bounded on one side by temperature and on the other by entropy. Like many other physical quantities, heat is detected only by the effect it produces *after* it has flowed. For example, we measure the temperature change of a medium resulting from the addition of heat and from such measurement learn something about the quantity of heat that produced the change. So it is with entropy. We are able to determine the entropy of a quantity of heat only from the effect the heat flow produces on a medium. *Since entropy is a factor of heat, whenever heat flows there is always an entropy change of the medium involved.* When the flow is *reversible* the entropy change produced in the medium *equals* the entropy of the heat delivered to or withdrawn from the medium. The necessity for stipulating reversibility as a requisite for the equality will be discussed later. For the present it is enough to say that for reversible processes we are able to determine the entropy of heat by reference to the medium to or from which it flows. It is the shift from the definition of entropy as a factor of heat to its measurement in terms of the change produced in a medium that has in the past been a source of trouble to the student.

It is an easy matter to determine the entropy of heat that flows reversibly and isothermally. The quantity of heat ${}_1Q_2$ that flows under such conditions may be computed from the mass of the medium, the ratios $\left(\frac{q}{dp}\right)_t$ or $\left(\frac{q}{dv}\right)_t$, and the pressure or volume change of the medium resulting from the flow. Since the flow is reversible the entropy of the medium is *changed* by the amount of the entropy of the heat that flows. Also, since we are considering an isothermal process, the temperature remains constant during the flow of heat. Then, by definition, the entropy of the heat quantity ${}_1Q_2$ is given by $S = \frac{{}_1Q_2}{T}$ units of entropy;* this value is the entropy *change* of the medium to or from which the heat flowed.

Because absolute temperature is always plus in sign, the algebraic sign of ${}_1Q_2$ governs the sign of the entropy change of a medium. If heat flows into a medium, ${}_1Q_2$ is plus and so is ΔS ; if heat leaves the medium,

* By definition, the units of entropy are $\frac{\text{units of heat}}{\text{units of absolute temperature}}$. Hence in the

British system of units, entropy is expressed in terms of Btu per degrees R. No specific name has ever been accepted for units of entropy.

${}_1Q_2$ and ΔS are both negative. From the point of view of the entropy of energy itself, the sign of S is always plus because any quantity of heat must have a certain positive dimension of entropy. Hence, variation in the algebraic sign of entropy has meaning only in reference to the entropy change of the medium to or from which heat flows.

Example

At a pressure of 165 lb per sq in. abs water evaporates at a constant temperature of 366° F. The latent heat of evaporation under these conditions is 857 Btu per lb. Determine the entropy change of 3 lb of water resulting from its reversible evaporation at this pressure and temperature.

Solution

The entropy change of the medium is given by

$$\Delta S = \frac{{}_1Q_2}{T}$$

The heat added ${}_1Q_2$ is the latent heat per pound times the number of pounds involved, i.e.

$${}_1Q_2 = 3 \times 857 \text{ Btu}$$

The constant absolute temperature T is

$$366 + 460 = 826^\circ \text{ R}$$

Then

$$\Delta S = \frac{3 \times 857}{826} = + 3.11 \text{ Btu/}^\circ \text{ R}$$

Since the process is reversible this value of ΔS is also the entropy S of the 3×857 Btu.

The expression of entropy as $\frac{{}_1Q_2}{T}$ suffers the limitation that it is applicable only to reversible isothermal processes. Only in such processes does the temperature remain constant. However, the entropy change for reversible non isothermal processes may be determined by use of the calculus. Suppose that, at any point in the change, the flow of heat is taken to be so small that the temperature may be considered to remain constant. Then in the limit

$$dS = \frac{\delta Q}{T}$$

in which δQ represents an infinitely small quantity of heat. But from the point of view of the medium the amount of heat that flows may be evaluated by

$${}_1Q_2 = Mc(t_2 - t_1)$$

which in this case becomes

$$\delta Q = Mc dt = Mc dT$$

Therefore, by substitution

$$dS = \frac{Mc dT}{T}$$

This differential expression depends only on temperature; therefore if we assume that the specific heat c remains constant, it may be integrated at once. When expressed as an indefinite integral the result is the absolute entropy of the medium, i.e.

$$S = \int \frac{Mc dT}{T} = Mc \log_e T + C$$

when c is taken to be constant. In order to evaluate the constant C , the value of S at the boundary condition of absolute zero of temperature must be known. Although there is some evidence for the determination of this boundary value, it need not be considered here. For practical purposes, all that is necessary is knowledge of the entropy change ΔS of a medium resulting from the reversible flow of a certain quantity of heat.

The value of ΔS is given directly by the definite integral of $Mc \frac{dT}{T}$

between the limits established by the absolute temperatures of the medium at the beginning and end of the process, T_1 and T_2 respectively.

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} Mc \frac{dT}{T} = Mc \int_{T_1}^{T_2} \frac{dT}{T} = Mc \log_e \frac{T_2}{T_1}$$

If the specific heat c is variable, the integral for ΔS may still be evaluated, although not as simply, by expressing c as $a f(t)$.

Example

Twelve lb of water are heated reversibly from 60° F to 190° F. If the specific heat of water is taken as 1.0, what is the resulting change in entropy of the water?

Solution

Since the temperature changes during the addition of heat, it is necessary to integrate $\frac{\delta Q}{T}$ to obtain the change in entropy.

$$\begin{aligned} \Delta S = S_2 - S_1 &= \int_{460+60}^{460+190} Mc \frac{dT}{T} = 12 \times 1 \int_{520}^{650} \frac{dT}{T} = 12 \times 1 \times \log_e \frac{650}{520} \\ &= 12 \times 1 \times \log_e 1.25 = 12 \times 1 \times 0.2235 \\ &= 2.68 \text{ units of entropy} \end{aligned}$$

The fact that the differential expression for entropy change may be integrated without knowledge of the way the change is effected indicates that entropy is a point function. Therefore, values of entropy change may be and are tabulated in terms of the coordinates for each of the thermodynamic media used in industry. Because entropy of a medium is determined by its state as defined by its thermodynamic coordinates, it may itself be used as a coordinate. In Chapter 1 it was stated that any

two of the coordinates p , V , and T suffice to fix the state of a medium. That statement may now be enlarged to say that knowledge of any two of the quantities p , V , T , and S is enough to determine the state. Therefore, a diagram of which T and S are the coordinate axes may be set up, a point on this diagram defines the state of a medium just as surely as does a state point on the pV diagram.

As an illustration of the way in which the temperature-entropy (TS) diagram may be used, let the processes of the Carnot cycle be represented on it (Fig. 3-6). The reversible isothermal expansion at the higher temperature T_1 is shown by 1-2. Since heat is added on this

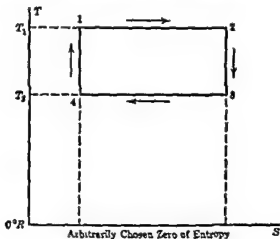


FIG. 3-6 Carnot Cycle— TS Plane.

change, the entropy of the medium increases, and by the definition of entropy, the area under 1-2 is a quantitative measure of the amount of heat added. The next change of the cycle is the reversible adiabatic expansion. The entire absence of any heat flow on this change requires that the line representing the change on the TS diagram shall not have any area under it. Thus the adiabatic expansion to T_2 must be represented by the vertical line 2-3. From the diagram, this line evidently represents a change at a constant entropy. It follows that a reversible adiabatic change is also isentropic, i.e., at constant entropy. The line 3-4 represents the reversible isothermal compression at the lower temperature T_2 , during which unavailable heat is rejected from the system. Since entropy is a factor of heat, the departure of heat from the system means that the entropy of the system must decrease as shown. The area under 3-4 is a graphic representation of the amount of heat rejected. The reversible adiabatic compression 4-1 then restores the medium to its initial state without change of entropy.

The first of several things to be learned from Fig. 3-6 is that the *entropy change of the system* resulting from the addition of heat is exactly equal and opposite in sense to that accompanying the rejection of heat. Therefore, the net entropy change for the entire reversible cycle is zero.

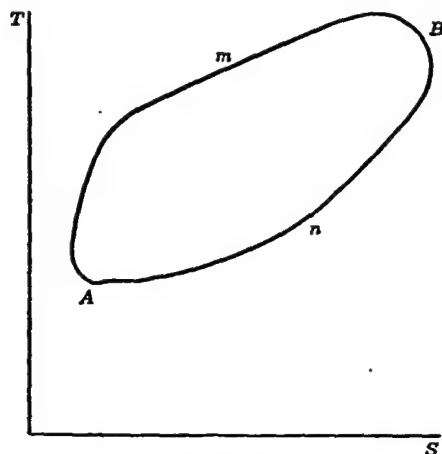


FIG. 3-7.

The same result would have been obtained even though there had been a change in temperature during either the addition or the rejection of heat, provided the cycle remained reversible (Fig. 3-7). Such a condition would require the use of the differential expression for change in entropy, i.e.

$$dS = \frac{McdT}{T}$$

The limits for the integration of dS over the path AmB representing addition of heat are T_B and T_A . For integration over BnA the limits are T_A and T_B . Hence the integral of dS over the closed path $AmBnA$ is identically equal to zero. Thus

$$\begin{aligned} \oint dS &= \int_{T_A}^{T_B} \frac{McdT}{T} + \int_{T_B}^{T_A} \frac{McdT}{T} \\ &= Mc \left(\log_e \frac{T_B}{T_A} + \log_e \frac{T_A}{T_B} \right) = 0 \end{aligned}$$

Note: The sign \oint means that the integral is to be taken over the complete closed path from A to B and back to A .

From this analysis it follows that it makes no difference through what series of changes a medium may go in a closed cyclical process; entropy at the end of the cycle is the same as it was at the beginning. Consequently, entropy of a medium is determined by the coordinates of the

state of the medium and not at all by the path by which it achieved that state. This demonstrates again that *entropy is a point function*.

It is to be noted carefully that it is only for reversible cycles that the entropy change of the medium resulting from heat addition is equal and opposite to the entropy change of heat rejection. *It is not true for irreversible cycles.* The conclusion is then readily drawn that the degree to which a cycle is irreversible is determined by the amount of the inequality of the entropy changes accompanying the addition and rejection of heat respectively. This is the reason behind the frequently encountered expression, "Entropy is the measure of irreversibility." This statement is meaningful only when considered in the light of a discussion such as the present one. The possibility of confusion if it is interpreted otherwise comes from the fact that *any flow of heat results in a change in entropy*. For example, if heat is added to a system isothermally and reversibly there is certainly an increase in the entropy of the system. But it was stated that the process was reversible. Therefore it is silly to say that in such a process increase in entropy is a measure of irreversibility. The point is that, in a cyclical process, it is the *inequality* between entropy changes resulting from the addition and rejection of heat respectively that tells us a cycle is irreversible and by how much.

The second point of interest in connection with Fig. 3-6 is that the enclosed area 1-2-3-4 on the TS diagram represents the difference between the heat supplied and that rejected. It must therefore be exactly equivalent to the net work done by the cycle. Consequently, with proper allowance for conversion and scale factors, it is equivalent to the area enclosed by the curves of the cycle on the pV diagram. The TS and pV diagrams studied together give a ready means of gaining a real understanding of what happens with respect to energy transformation for each change in the Carnot cycle.

Third, an adaptation of Fig. 3-6 yields the answer to the exceedingly important question. Since heat may be represented by area on the TS diagram, is the converse always true, i.e., does area on the diagram always represent heat? The answer to this question is an emphatic *No!* Fig. 3-8 is a reproduction of Fig. 3-6, except that the adiabatic expansion is irreversible instead of reversible. The dotted line is *not* to be considered as the path over which the change takes place, because the exact path of an irreversible process cannot be determined. Suffice it to say that the dotted line shows that the medium undergoes an adiabatic change of state from state 2 to state 3' for which the functional relation between T and S is not known. The irreversibility of the change 2-3' implies that turbulence and internal friction occur within the medium.

as the change takes place. Because of these friction effects, at any given instant there are points within the medium at different temperatures. This results in a flow of energy as heat from one point to another *within* the medium. Although this flow of heat is unknown in amount, it is irreversible heat flow and results in a definite increase in entropy.

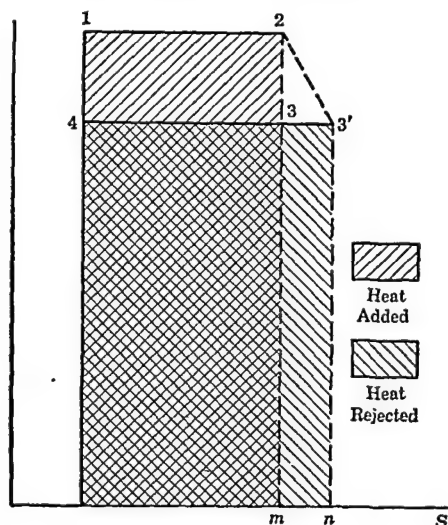


FIG. 3-8. Entropy Increase with Irreversible Adiabatic Expansion—TS Diagram.

Consequently, for the whole irreversible change, the entropy of the system increases from 3 to 3'. *It cannot be said that the area under 2-3' represents heat*, because, first, the fact that the process is adiabatic means that there is no heat flow to or from the surroundings, and second, it is impossible to know the exact path of the change and so it is absurd to talk about the area under it. Therefore, *area on a TS diagram represents heat quantity only for reversible changes*.

Finally, Fig. 3-8 shows beyond question that the presence of an irreversible change in a cycle inevitably leads to decreased efficiency in the transformation of heat into work. The area under line 1-2 represents, as before, the heat added to the system. But in order to complete the cycle reversible isothermal compression must now be started at point 3' instead of 3, and so the heat rejected is represented by the area under 3'-4. This area is greater than that under 3-4 by the area 3 3' nm. Hence, in the irreversible cycle, the heat that may be transformed into work is less than that transformed in the reversible cycle by the amount represented by 3 3' nm.

Summary of the Properties of Entropy

1 Entropy is the extensive factor of heat energy. For a reversible process, when change of entropy of a medium is multiplied by absolute temperature, the product is the heat quantity that flows during the change.

2 Entropy is a point function. In any reversible process, change in entropy depends only upon the initial and final state points of the medium. For a reversible isothermal change

$$\Delta S = \frac{1Q_2}{T}$$

For all other reversible changes except adiabatic

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{McdT}{T} = Mc \log_e \frac{T_2}{T_1}$$

3 Entropy may be used as a thermodynamic coordinate. It was established that entropy is determined by the state of a medium. It may therefore in its turn be used to identify the state.

4 Entropy of the medium changes whenever heat flows and the algebraic sign of the entropy change is the same as that of the heat. This comes from the fact that in the expression $dS = \frac{\delta Q}{T}$, T denotes absolute temperature which is always positive.

5 Entropy of a medium may be considered as a property of that medium as well as a dimension of energy. This is a consequence of the fact that entropy is determined by the coordinates of the state of the medium.

6 The entropy change of a system of several bodies is obtained by the algebraic addition of the entropy changes of the constituent bodies. The reason behind this statement is that entropy may be considered as much a property of the medium as its mass. Just as the mass of a system is the sum of the masses of its component parts, so is the entropy change of a system the algebraic sum of the entropy changes of its components.

7 Relative values of entropy are always used. Integration of the expression $S = \int \frac{McdT}{T}$ as an indefinite integral to obtain the absolute value of S involves an additive constant, the value of which is indeterminate. Therefore, for practical purposes, entropy is reckoned to an arbitrary datum established by some standard state. In the steam tables, for example, the entropy at 32° F is taken as zero, and the tabulated values represent the entropy above this datum.

Use of Entropy

Knowledge of the entropy of a quantity of heat makes it possible to compute the fraction of that heat that may be transformed into work in a reversible cycle. The way in which this is done may first be illustrated by reference to the Carnot cycle.

The equation that defines Carnot efficiency is

$$\eta_{\text{Carnot}} = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

$$= 1 - \frac{T_2}{T_1}$$

In terms of the nomenclature used in Fig. 3-9, this becomes

$$\eta_{\text{Carnot}} = \frac{Q_S - Q_R}{Q_S} = \frac{T_S - T_R}{T_S}$$

$$= 1 - \frac{T_R}{T_S}$$

The heat added to the cycle, Q_S , is represented on the diagram by the area 1-2-5-6. The heat rejected to the refrigerator, Q_R , is represented by the area 3-4-6-5.

Since Q_R cannot be transformed into work in this particular cycle it is called the *unavailable* part of the heat supplied.

The area 1-2-3-4, which is the difference between the areas representing Q_S and Q_R , represents the heat transformed into work, Q_A . Since Q_A is the *maximum* amount of heat that can be transformed into work by any cycle operating between T_S and T_R , it is called the *available* part of the heat supplied, or referred to simply as the available energy.

From the efficiency equation

$$Q_A = Q_S \eta_{\text{Carnot}} = Q_S \left(1 - \frac{T_R}{T_S} \right) = Q_S - \frac{Q_S}{T_S} \times T_R$$

But Q_A is also given by

$$Q_A = Q_S - Q_R$$

$$\text{Hence } Q_S - Q_R = Q_S - \frac{Q_S}{T_S} \times T_R$$

$$\text{So } Q_R = \frac{Q_S}{T_S} \times T_R$$

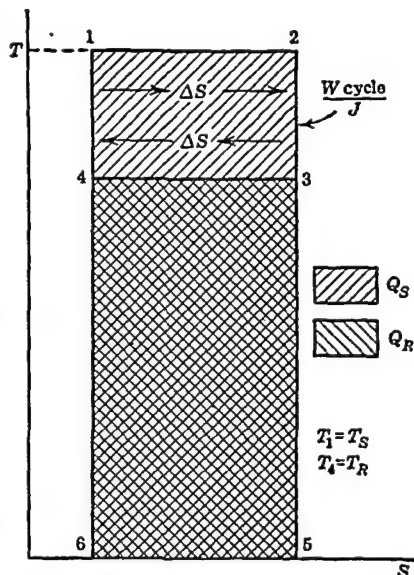


FIG. 3-9. Carnot Cycle—Representation of Heat Quantities on the TS Diagram.

purposes it may be considered as totally unavailable. Hence the word "lost" may be interpreted as meaning "unavailable." Mechanical energy is likewise degraded and "lost" by being transformed into heat as the result of turbulence and internal fluid friction within the medium itself. Because both external and internal frictional effects involve degradation of mechanical energy, they are respectively termed the causes of *external and internal mechanical irreversibility*. They are both minimized by giving attention to matters of design so that the lowest possible amount of high grade, 100% available mechanical energy of zero entropy will be transformed into low-grade, virtually unavailable heat energy. The reduction of external mechanical irreversibility is the object of modern highly specialized studies in lubrication and in the design of anti friction bearings. Internal mechanical irreversibility is diminished by reducing turbulence in the flow of the medium. This is accomplished by streamlining the passages through which the medium flows and by machining and even polishing the metal with which it comes in contact.

The computation of the loss of availability in both externally and internally mechanically irreversible processes is effected by obtaining the difference between the input and output of mechanical energy. This difference represents the energy transformed into heat. Its entropy is readily obtained by determining the entropy change of the medium to which it passes. Since the mechanical energy transformed was 100% available, it was of zero entropy. Therefore the entropy of the resulting heat represents the entropy increase caused by the irreversible process. Its product with the lowest available absolute temperature yields the amount of energy irretrievably wasted.

The second physical influence which causes irreversibility is not as obvious as the first, yet the fact that it is not so self-evident enhances its importance. In the preceding discussion the point was stressed that it was the transformation of high grade mechanical energy into low grade heat energy that constituted the irreversible and undesirable feature of friction. In conformity with the Second Law, all transmission of heat energy is from hot to cold and hence is inherently irreversible. It is only by setting up the abstract ideal of a reversible isothermal process that we can even imagine reversible heat transfer. So it is that the second type of irreversibility is thermal in character, for it has to do with heat transfer. Like mechanical irreversibility, it may be classified as *internal or external thermal irreversibility*.

Internal thermal irreversibility is exemplified by the mixing of two fluids initially at different temperatures, a process common enough in

calorimetry. Heat flows from the hotter to the colder of the two fluids until an equilibrium temperature is reached. Certainly the process is irreversible, for it is inconceivable that by an infinitesimal change of any coordinate the mixture could be caused to separate into its components, with each at its initial temperature. There is just as much energy in the mixture as there was in its two components, but because of the mixing, it is decidedly less available than it was before. The method of quantitatively determining the amount of the increase in unavailability is illustrated by the following example.

Example

If 10 lb of air at 3000° R are mixed at constant atmospheric pressure with 30 lb of air at 800° R, what is the change in entropy resulting from the mixing process? Also what is the change in availability, with respect to a refrigerator at 40° F, of the heat energy imparted to the mixture by the hot air?

Solution

The temperature resulting from the mixing may be determined by the method of mixtures, 0.24 being used as the specific heat of air at constant pressure. Thus

$$10 \times 0.24 \times (3000 - T) = 30 \times 0.24 \times (T - 800) \\ T = 1350^\circ \text{ R}$$

The amount of heat that leaves the hot air is wholly absorbed by the cold air; hence the total heat quantity transferred is

$$10 \times 0.24 \times (3000 - 1350) = 3960 \text{ Btu}$$

If this quantity of heat had been withdrawn from the hot air reversibly, its entropy would have been

$$10 \times 0.24 \log_e \frac{3000}{1350} = 1.916 \text{ units of entropy}$$

Now let us compute the entropy of the same quantity of heat yielded by the hot air if it is withdrawn reversibly from the mixture. This withdrawal would result in a reduction in the temperature of the mixture to a value that may be computed as follows

$$3960 = 40 \times 0.24(1350 - T_1) \\ T_1 = 937.5^\circ \text{ R}$$

The entropy of the 3960 Btu when withdrawn from the mixture is therefore

$$40 \times 0.24 \log_e \frac{1350}{937.5} = 40 \times 0.24 \times 0.365 \\ = 3.504 \text{ units of entropy}$$

When this value is compared with the entropy for the same amount of heat energy when supplied by the hot air, it appears that the mixing process has

resulted in an increase in entropy of 1.588. Hence the increase in unavailability of energy with respect to a 40° F refrigerator is

$$1.588 \times 500 = 794 \text{ Btu}$$

or about 20% of the total amount of energy in question!

Probably the most important of all types of irreversibility is that encountered when heat is added to a medium from an external source. Inasmuch as it is only by combustion that we can release the chemical energy stored in natural resources, the temperature at which heat first manifests itself must inevitably be that of combustion. In many cases, however, it is not possible to provide a medium capable of absorbing the heat at anything like that temperature. Consequently, the heat flows down a considerable temperature gradient before it is delivered to the medium, with a resulting increase in entropy and loss in availability. The question immediately arises: Is this effect great enough to be significant? The answer is given by comparative entropy computations as illustrated in the following example.

Example

At a pressure of 120 lb per sq in., the warming of water from 32° F to the boiling temperature and subsequent complete evaporation requires 1190 Btu per lb. At this pressure the boiling point of water is 341° F. The combustion of the fuel maintains a temperature of 2800° F in the firebox of the boiler.

(a) Compute, as the heat leaves the firebox, the entropy of the energy required to warm and evaporate 1 lb of water at the designated pressure.

(b) Compute the entropy of the same quantity of heat if it were withdrawn reversibly from the steam.

(c) What is the amount of the decrease in availability (40° F receiver) of the heat supplied per pound of steam by reason of the irreversible heat transmission?

Solution

The 1190 Btu required to warm and evaporate 1 lb of water is at a temperature of 2800° F as it leaves the fire. Its temperature is reduced to a maximum of 341° F by its passage through the walls of the boiler tubes and its addition to the water. Clearly such a process is highly irreversible. By no means except by the expenditure of a great deal of work can it be conceived that the heat after transmission could be made to return to its original high temperature of 2800° F.

(a) The heat required to warm and evaporate 1 lb of water (1190 Btu) leaves the fire isothermally at a temperature of 2800° F = 3260° R. Therefore the entropy of this amount of energy is given by

$$\frac{Q_1}{T} = \frac{1190}{3260} = 0.365$$

(b) The next question involves the entropy increase of the water as a result of the addition of the heat to it. This is equal to the entropy of the same amount of heat if withdrawn *reversibly* from the water. Since the temperature changes during the warming from 32° F to the boiling point, the entropy change of the warming is given by the formula

$$\Delta s = Mc \log_e \frac{T_2}{T_1}$$

$$\begin{aligned} \text{warming} &= 1 \times 11 \log_e \frac{341 + 460}{32 + 460} \\ &= 6.68461 - 6.19848 = 0.48613 \end{aligned}$$

The evaporation of the water takes place isothermally at a temperature of 801° R, and the latent heat of evaporation at the designated pressure is 877.4 Btu per lb. Hence the entropy change for evaporation is given by

$$\Delta s_{\text{evaporation}} = \frac{q_{\text{evap}}}{T} = \frac{877.4}{801} = 1.095$$

Therefore the sum of the entropy changes of warming and evaporation is

$$\Delta s_{\text{warming}} + \Delta s_{\text{evaporation}} = \Delta s = 1.095 + 0.48613 = 1.58113$$

From this analysis it appears that the 1190 Btu has an entropy of 0.365 when it leaves the fire, and an entropy of 1.58113 after it enters the medium.

(c) Now suppose that the heat were to be used in each of these two cases in a *reversible* cycle, of which the receiver or cold body is at a temperature of 40° F. If the heat could have been used at the high firebox temperature, the unavailable energy would have been

$$Q_{\text{unavailable}} = T_R \frac{q_2}{T_2} = 500 \times 0.365 = 182.5 \text{ Btu per 1190 Btu supplied}$$

On the other hand, the heat actually is used in a cycle in which steam is the medium. If, for the sake of comparison, this cycle is considered reversible and as having a condenser at a temperature of 40° F, the unavailability is

$$Q_{\text{unavailable}} = T_R \Delta s = 500 \times 1.58113 = 790.6 \text{ Btu per 1190 Btu supplied}$$

Hence, because of the inability of water to absorb heat at the high temperature of the firebox, the resulting irreversible heat transmission has caused a decrease in availability amounting to $790.6 - 182.5 = 608.1$ Btu per 1190 Btu, or per pound of steam used.

Use of Point Functions in Evaluating ${}_1Q_2$ and ${}_1W_2$

The study of entropy and its use reveals that under certain *well-defined limiting conditions* entropy, a point function, may be profitably used in the evaluation of heat, a path function. A prime objective of thermodynamics is the evaluation of ${}_1Q_2$ and ${}_1W_2$ for all kinds of state changes. Both of these quantities have been shown to be path functions. However, if point functions can be found which, for certain commonly encountered types of change, can be related to either ${}_1Q_2$ or ${}_1W_2$, a considerable

increase in the facility of evaluating these quantities will be achieved. It must be kept clearly in mind that any point function can be related to either ${}_1Q_2$ or ${}_1W_2$ only for one certain type of change. If a relationship could be established for more than one type of change it would mean that ${}_1Q_2$ or ${}_1W_2$ was equal to the point function over two different paths. This would be proof that ${}_1Q_2$ and ${}_1W_2$ were independent of path and were point functions themselves, which they most definitely are not¹.

Two point functions which are useful in the evaluation of ${}_1Q_2$ and ${}_1W_2$ have already been studied, i.e., intrinsic energy and enthalpy. There are two others, maximum work and free energy, which are no less useful. Their definition and the discussion of their significance and use must wait, however, until the use of intrinsic energy and enthalpy in the present connection has been described.

First, consider a non flow constant-volume change. No work is done on such a change, for dV is zero and so $\int p dV = 0$. Therefore the Non-Flow Energy Equation becomes

$$J_1Q_2 = E_2 - E_1 + \int_{v_1}^{v_2} p dV]_{-0} = E_2 - E_1 \text{ in ft-lb}$$

In this case the heat added to or withdrawn from the medium is equivalent to the change in intrinsic energy. Since the latter is a point function, values for it may either be found in tables or be determined from knowledge of the coordinates of the initial and final state points. *For any non-flow constant-volume change, then, the heat flow to or from the medium is measured by the simple difference between the values of intrinsic energy for state 2 and state 1.*

The Non-Flow Energy Equation for a reversible adiabatic change also reduces to two terms, one a point and the other a path function, as follows

$$J_1Q_2 = (E_2 - E_1) + {}_1W_2$$

For a reversible adiabatic change ${}_1Q_2 = 0$

So $0 = (E_2 - E_1) + {}_1W_2$

or ${}_1W_2 = \int_{v_1}^{v_2} p dV = - (E_2 - E_1) = E_1 - E_2$

Consequently, the work done on a non-flow reversible adiabatic change is measured by the negative difference between the values of intrinsic energy for state 2 and state 1.

It has already been suggested (see above) that the point-function enthalpy may be conveniently used in the evaluation of either ${}_1Q_2$ or

${}_1W_2$ over a particular path. In order to see what can be done in this direction, let the equation defining H be differentiated, i.e.

$$H = E + \frac{pV}{J}$$

$$dH = dE + \frac{p dV}{J} + \frac{V dp}{J} \quad (1)$$

For comparison, also differentiate the Non-Flow Energy Equation

$$JQ = E + \int_1^2 p dV$$

$$J \delta Q = dE + p dV$$

or

$$\delta Q = dE + \frac{p dV}{J} \text{ in heat units} \quad (2)$$

By substituting this value for its equal in Equation (1) we have

$$dH = \delta Q + \frac{V dp}{J}$$

or, when the definite integral is taken

$$H_2 - H_1 = {}_1Q_2 + \int_{p_1}^{p_2} V dp$$

Hence, in non-flow processes the change in H between two states is equal to the heat flow to or from the medium plus $\int_{p_1}^{p_2} V dp$. It is evident that $\int V dp = 0$ when $dp = 0$, a condition which characterizes a constant-pressure change. Therefore, the difference between the tabulated values of H for two different states measures the heat flow to or from the medium, if the change is non-flow and is made at constant pressure.

The great usefulness of the enthalpy function in determining ${}_1Q_2$ or ${}_1W_2$ in certain flow processes has already been described (pages 32-36) in examples illustrative of the application of the General Energy Equation. The enthalpy function is also widely used in chemistry to denote the *heat of a chemical reaction*. When used in this connection, the intrinsic energy factor in the definition of enthalpy must be taken to include both atomic and molecular energy, i.e., the sum of the terms $C + E$ as used in this book. This difference in nomenclature between engineering and chemical thermodynamics is apt to be confusing. It arises because chemistry is concerned with heat resulting from the reaction of *two or more* media. On the other hand, until the comparatively recent detailed thermodynamic study of internal combustion engines, engineering processes and cycles have been concerned with the properties of only *one* medium.

The two other point functions that have been found useful in determining ${}_1Q_2$ and ${}_1W_2$ for certain changes are *maximum work* (W_{\max}) and

free energy (F) Free energy, moreover, has special application in chemical thermodynamics, for knowledge of its value is extremely useful in determining the conditions for the equilibrium of a chemical system

The definition of the function W'_{\max} is given by the equation

$$W'_{\max} = E - TS$$

In this definition E is to be considered as including both chemical energy C and molecular energy E , in accordance with the convention used by chemists. Its physical significance is best appreciated by differentiation of the equation and by the physical identification of each of the resulting components, thus

$$dW'_{\max} = dE - TdS - SdT$$

If the process is isothermal, the negative term SdT becomes zero. Further, if the process is also reversible, $TdS = \delta Q^*$

Then
$$dW'_{\max} = dE - \delta Q$$

or
$$\delta Q = dE - dW'_{\max}$$

As written thus, the equation is in heat units. If $-dW'_{\max}$ is taken as equal to $+\frac{dW'}{J}$, the equation then reduces to the Non Flow Energy Equation expressed in heat units. As it stands, it was derived from the W'_{\max} function for a reversible isothermal change. From study of the Carnot cycle, a *maximum* amount of work is done when heat is added to a medium isothermally and reversibly. Therefore the name of the function W'_{\max} is justified.

It is profitable to consider further the significance of taking $-dW'_{\max}$ equal to $+\frac{dW'}{J}$. The function W'_{\max} is taken to mean that any substance in any particular state possesses a maximum capacity to do work as it passes to some other state. This must not be confused with the intrinsic energy of the substance, because, by definition, W'_{\max} includes energy over and above intrinsic energy. As the substance changes state reversibly and isothermally, the external effect produced is equal in amount and opposite in sign to the change in the values of W'_{\max} for the initial and final states. For example, on an expansion, W'_{\max} is positive. The change in W'_{\max} must be negative because after the expansion the medium has less capacity for doing work.

Since at any given state point there can be but *one value* for the *maximum* ability of a substance or system to do work, W'_{\max} is a point function.

* This equation may be called the mathematical expression of the Second Law

As such, the difference between its values at two state points measures and is the negative of ${}_1W_2$ for a *reversible isothermal change*.

If a system undergoes an irreversible change of state, the negative of the change in the maximum work function W_{\max} is no longer equal to the external work done. The actual change in the function is the same as before, but the irreversibility of the process prevents the realization of ΔW_{\max} as external work.

The significance of W_{\max} and its relationship to a reversible process may seem abstract to the student, inasmuch as all natural processes are irreversible rather than reversible. It is, however, in the field of electrochemistry that an approximate approach to a reversible process can be made. Fig. 3-11 shows a schematic arrangement of an electrochemical cell with a motor in the external circuit. Let the cell be placed in a thermostat in order to keep the temperature constant. If R is the resistance of the external circuit and i the current flowing, heat is evolved at the rate of Ri^2 and work is done on the motor at the rate of $\mathcal{E}i - Ri^2$, where \mathcal{E} is the emf of the cell. As i is reduced in magnitude, the second term approaches zero more rapidly than the first, and the circuit becomes reversible in the measure that Ri^2 approaches zero. Suppose that the current flowing is reduced to such a point as to make the cell approximately reversible. Then the amount of electrical work done by the motor measures the isothermal reversible work obtained from the electrochemical

reaction in the cell, *provided there is no volume change because of the reaction*. Under these conditions, the amount of work done by the motor is equivalent to the decrease of the W_{\max} function for the system. If the elements of the cell are permitted to react irreversibly in a beaker, the change in the W_{\max} function will be the same as it is when the reaction takes place in the reversible cell. The external work done, however, is zero if there is no difference between the volume of the reactants and the products of the reaction. The conclusion is that any change in a system results in a definite single-valued change in the W_{\max} function. The energy represented by the change in W_{\max} is actually realized as external work ${}_1W_2$ to the degree that the change of state approaches a reversible isothermal process.

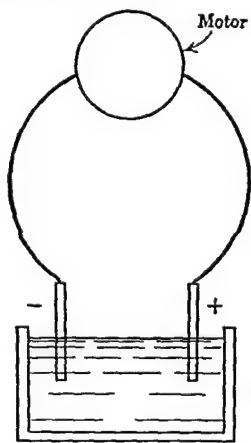


FIG. 3-11. Schematic Arrangement of an Electrochemical Cell with Motor in External Circuit.

Total resistance of circuit $= R$.

Heat evolved in overcoming resistance $= Ri^2$.

Free energy, the fourth point function of those that may be related to ${}_1Q_2$ or ${}_1W_2$, is an extension of the W_{\max} function. Anyone who has had any experience in chemistry will realize that chemical reactions are generally accompanied by changes in volume. There may be evolution of gas as a result of the reaction or, if the reactants are solutions, there may be appreciable changes in the volume of liquid involved. Since chemical reactions are usually carried on at constant atmospheric pressure, some of the energy derived from the reaction must be utilized to provide space for the volume change against the pressure acting. It was Willard Gibbs who first saw the necessity for considering this amount of energy in the determination of the maximum work actually to be derived from any chemical change. With reference to the reversible electrochemical cell discussed in connection with the W_{\max} function, free energy may be defined as the *maximum amount of external work delivered by the motor*. But *some* external work has to be done at the cell itself in order to provide the space necessary for the change to go on. Both the work per second, \dot{E} , of the motor and the work, $\frac{p\Delta V}{J}$, to provide space were done at the expense of the maximum work content of the system. Consequently, while W_{\max} indicates the maximum work content of a system, the full value of its change is not realizable as useful external work even in a reversible isothermal process *if a volume change accompanies that process*. Hence the difference between W_{\max} and free energy F is the amount of work that has to be done in order to provide space for the products of reaction. Account is taken of this difference by defining free energy by the equation

$$F = E - TS + \frac{pV}{J}$$

Free energy is a point function, for its definition shows that it is the algebraic sum of intrinsic energy, a point function, TS , the product of two coordinates, and pV , the product of two other coordinates. Its value, therefore, may be uniquely determined from knowledge of the *coordinates of the state of a system*. The limiting conditions under which $-\Delta F$ measures external work are as follows

- 1 The change must be reversible
- 2 The change must be carried out under isothermal conditions.
- 3 The change must also be carried out at constant pressure

The necessity for these conditions may be seen by differentiating the equation

$$F = E - TS + \frac{pV}{J}$$

Thus

$$dF = dE - TdS - SdT + \frac{pdV}{J} + \frac{Vdp}{J}$$

If the change is isothermal, SdT vanishes. If it is at constant pressure, Vdp likewise vanishes. Finally, if the change is reversible, it is possible to substitute δQ for TdS . There results

$$dF = dE - \delta Q + \frac{pdV}{J}$$

In the discussion of W_{\max} it was demonstrated that for a reversible isothermal change

$$dE - \delta Q = dW_{\max}$$

Hence

$$dF = dW_{\max} + \frac{pdV}{J}$$

From the definition it would appear that the result should be that the free-energy change equals the *difference* between the change in W_{\max} and the external work done. Yet the above equation gives dF equal to the algebraic sum of dW_{\max} and $\frac{pdV}{J}$. This apparent contradiction is not as bad as it looks. A little reflection on the matter brings the realization that both W_{\max} and free energy are energy *contents* of the reacting system, whereas $\frac{pdV}{J}$ refers to work done on or by the surroundings. The algebraic sign of change in energy content must necessarily always be opposite to that for external work done. Consider, for example, a reaction that takes place spontaneously. Both W_{\max} and free energy *decrease* as the system goes from state 1 to state 2. If this were not so, the change would not take place. Hence in the above equation it is proper to write both dF and dW_{\max} with negative signs to indicate that if the reaction takes place it is accompanied by a decrease in both of these quantities; thus

$$-dF = -dW_{\max} + \frac{pdV}{J}$$

This equation is now in agreement with the idea that the free-energy change equals the difference between the change in W_{\max} and the work done in providing space for the products of the reaction.

It must be emphasized that all four of the quantities E , H , W_{\max} , and F are concerned with energy *contents* of the system under discussion. If this energy is utilized to produce external effects, the particular energy

content under discussion undergoes a decrease. Conversely, if the external surroundings produce an effect upon the system, the result is an increase of the particular energy content in question. The student must get a clear conception of the essential difference between the energy content of the system and the changes produced on the surroundings, or by the surroundings, as a result of a change in that energy content.

A homely and naïve illustration of the meaning of these remarks may be given by considering energy changes that take place in the human body. As the result of eating a meal, a man's energy content is increased. Suppose that after eating the meal he works in his garden. His energy content is decreased. As a result of the work done in the garden he has produced an external effect at the expense of a decrease in energy content. Of course, the human body does not operate on a reversible cycle, and so the amount of work done in the garden is not equal to the decrease in energy content.

As a means of obtaining a better idea of the significance and usefulness of all four of the quantities E , H , W_{\max} , and F , consider the information they yield when applied to a simple chemical reaction. For example, let a piece of zinc be placed in a hydrochloric acid solution. A vigorous reaction immediately results, accompanied by the evolution of hydrogen. If the beaker containing the solution is touched, it will be found to be warm. Evidently heat is being given off by the reaction. The ultimate cause of the reaction is the difference in the energy possessed by the system zinc and hydrochloric acid and the system zinc chloride and hydrogen. Hence the intrinsic energy (chemical definition) has decreased as a result of the reaction. If the beaker containing the reactants is open to the atmosphere, the process is carried on at constant pressure. Then the application of the Non Flow Equation gives

$$J_1 Q_2 = (E_2 - E_1) + {}_1W_2$$

Since E decreased in going from state 1 to state 2, ΔE is negative. The only work that has been accomplished by the reaction has been the work done to provide space for the evolution of hydrogen, equal to the atmospheric pressure times the change in volume, i.e., $p(V_2 - V_1)$. Because this work was done on the surroundings, its sign is positive. The fact that heat can be detected as being given off makes the sign of $J_1 Q_2$ negative, and so the Non-Flow Equation with appropriate signs is

$$-J_1 Q_2 = -\Delta E + {}_1W_2$$

It has already been established that heat flow to or from the surroundings in a non-flow process carried on at constant pressure is measured

by the change in the enthalpy H . Just as the reaction caused a decrease in the intrinsic energy, so will it cause a reduction in enthalpy. Therefore, H_1 is greater than H_2 , and $H_2 - H_1$ is negative, i.e.

$${}_1Q_2 = -\Delta H = H_1 - H_2$$

If H_1 and H_2 are known, ${}_1Q_2$ may be computed. Conversely, the measurement of ${}_1Q_2$ in a constant-pressure calorimeter makes possible the experimental measurement of the difference between H_1 and H_2 .

The zinc-hydrochloric acid reaction might have been carried out in an electrolytic cell, with zinc and hydrogen as electrodes and the hydrochloric acid solution as the electrolyte. If this cell had been placed in a thermostat and the external circuit completed through a motor, conditions would have been favorable for approaching reversibility. Under these conditions, if there were *no* volume change, the amount of work done by a motor placed in the circuit would have been equal to the decrease in the W_{\max} content of the reactants. If the electrolytic cell tends to cool off as the reaction proceeds, the maintenance of the isothermal condition requires that heat be added. This heat is transformed into work, together with the energy from the reaction itself. Conversely, if the cell tends to heat up in operation, the maintenance of the isothermal condition requires that heat be given off to the thermostat. Consequently less external work is done than is represented by the amount of heat evolved by the reaction.

The essential point is that with volume assumed to remain constant, *it is only when the entropy of the system is the same before and after reaction that the heat of reaction equals the decrease in W_{\max}* . But the constancy of entropy requires that the reaction be carried on reversibly as well as isothermally. When the zinc is placed in the hydrochloric acid in a beaker and the reaction allowed to proceed without interference, the process is highly irreversible. Considerable energy would be required to restore the products of the reaction to the state in which they were before reacting. A considerable change in entropy therefore accompanies the reaction and so the *heat of reaction is not equivalent to the decrease in the W_{\max} function*.

In what has just been said, a limitation has been placed on the process to the effect that there shall be no volume change. The fact that there is an evolution of hydrogen against the constant atmospheric pressure is evidence that the limitation is exceeded. Hence a certain part of the maximum work content must be utilized in providing space for the products of reaction. That being the case, the amount of work done by the motor in the external circuit is measured by the decrease in free-energy content, the reaction being carried out reversibly and at constant

temperature and pressure. The basis for determining the efficiency of the reaction is the maximum amount of energy left over for doing external work after space has been provided for the products of reaction.

A mechanical analogy, which must not be too closely drawn, may help to make this idea clear. A mass of water that weighs 100 lb and is at an elevation of 25 ft has a maximum capacity of doing work of $100 \times 25 = 2500$ ft lb. If the water is at zero elevation it has no capacity for doing work and is in equilibrium with the surroundings. In the first instance the water will fall spontaneously when it is released from its container because it is out of equilibrium with the surroundings. We say that the measure of the lack of equilibrium of the water is given by its capacity for doing work. Similarly, if a system of two or more chemicals is at a high potential level of free energy with respect to the free energy level of the products of their reaction, the reactants and products are *not* in equilibrium and the reaction may proceed spontaneously. If the free energy content of the reacting system is equal to that of the products system, reactants and products of reaction are in equilibrium. Finally, if the free-energy content of the products system is greater than that of the reacting system, the reaction will not take place until an amount of energy is supplied greater than the difference in the two values of free energy. These relationships between free energy and the possibility of chemical reaction may be summarized as follows:

If $\Delta F = F_2 - F_1$ is *negative*, spontaneous reaction may take place

$\Delta F = F_2 - F_1$ is *zero*, equilibrium results

$\Delta F = F_2 - F_1$ is *positive*, reaction is not possible unless energy is supplied from the surroundings

In consequence of these conditions for chemical reaction many writers describe free energy as "the driving force of a chemical reaction."

In the past, metallurgical practice has utilized heat of reaction as the basis for determining whether a given reaction will proceed. From what has been said here, this is clearly wrong. *Heat of reaction is not the same as free-energy change.* This may be seen quickly enough from

the definitions alone, i.e., heat of reaction $H = E + \frac{pV}{J}$, free energy $F = E - TS + \frac{pV}{J}$. The difference between these two quantities is

the amount of heat absorbed or rejected in order to keep the temperature constant. Finally, it must be realized that the heat of reaction can be determined calorimetrically. It is usually taken as the heat given off by a constant pressure reaction. The free-energy change can be determined

only by setting up an ideal reversible process. This limitation, however, in no wise impairs the usefulness of the free-energy idea, because *whether the reaction takes place reversibly or irreversibly*, the decrease in free-energy content is the same. Its complete utilization in an external circuit can be achieved *only* when the reaction is carried on reversibly. But in any event it is the decrease in free-energy content that drives the reaction to completion.

CONDITIONS UNDER WHICH THE POINT FUNCTIONS E , H , W_{\max} , AND F
MAY BE RELATED TO ${}_1Q_2$ AND ${}_1W_2$

Change in	Measures	On
E	Q	Non-flow constant-volume change
E	W	Non-flow adiabatic change
H	Q	Constant-pressure change, flow or non-flow
W_{\max}	W	Reversible isothermal change
F	W	Reversible constant pressure isothermal change

The Gibbs-Helmholtz Equation — Determination of ΔH and ΔF

The importance of identifying free energy, rather than heat of reaction, as the significant factor in determining chemical equilibria leads to the thought that it would be valuable to find some way of quantitatively determining the difference between ΔH and ΔF from experimental data. One means for doing this is provided by the Gibbs-Helmholtz Equation. The physical basis for the derivation of this equation is the electrolytic cell described previously (pages 87-88).

Suppose that the external circuit of the cell has been adjusted to make the current i so small that the cell is essentially reversible.

It has been shown that for a reversible constant-pressure isothermal change, the external work done is equal to the negative of the free-energy change. For a reversible electrolytic cell, the external work is done by the motor in the circuit. The voltage \mathcal{E} in the circuit may be measured, and the product of its value times the quantity of electricity that flows gives the electrical work done. In electrochemical calculations the unit quantity of electricity is the faraday, which is equal to 96,500 coulombs per gram-atom equivalent of the active substances in the cell. The quantity of electricity that flows *per mol* is then obtained by multiplying by the valence, or number of gram-atom equivalents involved in the reaction. Hence the electrical work done by the motor per mol of reactants equals $n \times 96,500 \times \mathcal{E}$ which, when divided by 4.18, the cgs factor for conversion of joules to calories, gives as the value of $-\Delta F$ for the reversible reaction.

$$- \Delta F \text{ (in heat units)} = \frac{n \times 96,500 \times E}{4.18} \quad (1)$$

The heat of reaction is defined as the heat effect which occurs when a chemical reaction proceeds isothermally without useful work effect, i.e., irreversibly. While such a reaction may take place at constant pressure or at constant volume, the former case is the one of major practical importance. For such a constant pressure change, it has already been established that

$$[{}_1Q_2]_p = \Delta H$$

By definition
$$H = E + \frac{pV}{J} \quad (2)$$

and
$$F = E - TS + \frac{pV}{J} \quad (3)$$

thence
$$F = H - TS \quad (4)$$

If (4) is differentiated with respect to T with p constant, there results

$$\left(\frac{\partial F}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_p - S \quad (5)$$

To determine the value of $\left(\frac{\partial H}{\partial T}\right)_p$,
differentiate (2)

$$dH = dE + \frac{pdV}{J} + \frac{Vdp}{J} \quad (6)$$

From the Non-Flow Energy Equation

$$\delta Q = dE + \frac{pdV}{J} \quad (7)$$

Also

$$\delta Q = TdS \quad (8)$$

Thence, by substitution

$$dH = TdS + \frac{Vdp}{J}$$

For a constant-pressure process

$$dp = 0, \text{ and } dH = TdS$$

Substitution of this value for dH in (5) gives

$$\begin{aligned} \left(\frac{\partial F}{\partial T}\right)_p &= T\left(\frac{\partial S}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_p - S \\ &= -S \end{aligned} \quad (9)$$

Or, from (4)

$$\left(\frac{\partial F}{\partial T}\right)_p = -S = \frac{F - H}{T} \quad (10)$$

When equation (10) is applied to the free-energy *change* of reactants and products of reaction, both under the same restraint of pressure

$$\left(\frac{\partial(\Delta F)}{\partial T}\right)_p = -\Delta S = \frac{\Delta F - \Delta H}{T} \quad (11)$$

Solving this for $-\Delta H$ gives

$$-\Delta H = -\Delta F + T\left(\frac{\partial(\Delta F)}{\partial T}\right)_p \quad (12)$$

It was shown above that

$$-\Delta F = \frac{n \times 96,500 \times \varepsilon}{4.18}$$

Substituting this value in (12) gives one form of the Gibbs-Helmholtz Equation, i.e.,

$$\begin{aligned} -\Delta H &= -\Delta F + T \frac{\partial}{\partial T} \left(-\frac{n \times 96,500 \times \varepsilon}{4.18} \right) \\ &= -\Delta F - \frac{n \times 96,500}{4.18} T \left(\frac{\partial \varepsilon}{\partial T} \right)_p \end{aligned} \quad (13)$$

$$= + \frac{n \times 96,500 \times \varepsilon}{4.18} - \frac{n \times 96,500}{4.18} T \left(\frac{\partial \varepsilon}{\partial T} \right)_p \quad (14)$$

An example will illustrate how the above equations are used.

Example

For the reaction $\text{Cd} + \text{PbCl}_2 = \text{CdCl}_2 + \text{Pb}$, the voltage is 0.18801 volt at 25° C, and the change in voltage per unit change of temperature is -0.00048 . (a) Find the heat of reaction at 25° C, and (b) compare with the free-energy change.

Solution

(a) The valence of the reaction is 2; the absolute temperature T is $273 + 25 = 298^\circ \text{K}$. Substitution of these values in the Gibbs-Helmholtz Equation gives

$$\begin{aligned} -\Delta H_{\text{per mol}} &= \frac{2 \times 96,500}{4.18} [0.18801 - 298(-0.00048)] \\ &= 15,285 \text{ cal per mol} \end{aligned}$$

or $\Delta H_{\text{per mol}} = -15,285 \text{ cal per mol}$

The minus sign indicates that when the reaction takes place, heat is given off.

(b) The free energy change in calories for the reaction is

$$-\Delta F = \frac{n \times 96\,500 \times \mathcal{E}}{4.18} = \frac{2 \times 96\,500 \times 0.18801}{4.18} = 8680$$

or $\Delta F = -8680$ cal per mol at 25°C

Because ΔF is negative the reaction occurs spontaneously

Evidently for this particular reaction there is a considerable difference between the heat of reaction and the decrease in free energy, a difference that amounts to 6605 calories per mol. By subtracting the equation for $-\Delta F$ from that for $-\Delta H$ the difference might have been computed directly from

$$(-\Delta H) - (-\Delta F) = -\frac{n \times 96\,500}{4.18} T \left(\frac{\partial \mathcal{E}}{\partial T} \right)$$

Physically, the difference is accounted for by the fact that the cell made up of these particular reactants tends to heat up in operation, as is indicated by its *negative* temperature coefficient $\frac{\partial \mathcal{E}}{\partial T}$. Therefore, in order to maintain isothermal conditions 6605 calories per gram mol must be rejected from the system. Actually the driving force of the reaction is only about 57% of the observed heat of reaction, a difference which cannot be ignored.

For some reactions ΔH and ΔF actually differ in sign as well as in magnitude. The following example illustrates such a case and shows how important it is to use ΔF as the basis for predicting whether or not the reaction may take place.

Example

The temperature coefficient of the cell $\text{Ag} \mid \text{AgCl} \mid \text{HgCl} \mid \text{Hg}$ is $+0.000336$ volt per $^\circ\text{C}$ and the emf at 298°K (25°C) is 0.0455 volt. (a) What is the value of ΔH for the cell reaction? (b) What is the value of ΔF ? (c) Will the reaction take place spontaneously at 25°C ?

Solution

(a) From the Gibbs-Helmholtz Equation and the given data the value of ΔH is

$$-\Delta H_{\text{per mol}} = \frac{n \times 96\,500}{4.18} [0.0455 - 298(0.000336)]$$

The valence n of the cell reaction is 1, so

$$\begin{aligned} -\Delta H &= \frac{1 \times 96\,500}{4.18} (0.0455 - 0.10013) \\ &= -1260 \end{aligned}$$

or $\Delta H = +1260$ cal per mol

The plus sign of ΔH signifies that when this reaction is carried out in a calorimeter *heat is absorbed from the surroundings*.

(b) The value of ΔF for the cell reaction is given by

$$-\Delta F = \frac{n \times 96,500 \times \varepsilon}{4.18} = \frac{1 \times 96,500 \times 0.0455}{4.18}$$

$$-\Delta F = 1050$$

or $\Delta F = -1050$ cal per mol at 25°C

(c) Since the value of ΔF for the reaction turns out to be negative, *the reaction takes place spontaneously, even though the heat of the reaction ΔH is plus*. The fact is that, as the reaction proceeds, the cell tends to cool off, as is indicated by its positive temperature coefficient. That is, as the voltage of the cell decreases, the temperature likewise decreases, and so $\frac{\partial \varepsilon}{\partial T}$ is positive. Consequently, in order to maintain the isothermal condition, heat is absorbed from the surroundings and through the operation of the cell is delivered to the external circuit where it may be transformed into work. Because the reacting system possesses this ability to do work, it is above the energy level of the system made up of the products of reaction; hence the reaction occurs spontaneously.

Dependence of ΔE , ΔH , and ΔF on Temperature. The Third Law of Thermodynamics

The fact that E , H , W_{\max} , and F are point functions means that they are specified by any two coordinates of the state of a medium. Moreover, since any point function may itself be used as a coordinate, it is possible to write a considerable number of functional relationships for the specification of any one point function. Some of these are of greater practical usefulness than others because of their greater adaptability to experimental thermal data. In particular, since chemical equilibria are obviously affected by temperature, it is especially desirable to establish the functional relationships for H and F in terms of temperature. Because ΔH measures heat flow for a constant-pressure process, specific heat at constant pressure equals the rate of change of h per unit of temperature, i.e.

$$c_p = \left(\frac{q}{dt} \right)_p = \left(\frac{\partial h}{\partial T} \right)_p$$

or
$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \text{ per mol}$$

Hence, H is a function of temperature and of the specific heat at constant pressure. When C_p is variable, it also is a function of temperature and may be expressed as

$$C_p = a + bT + cT^2 + \dots$$

in which C_p is the molal specific heat, T is the absolute temperature, and a, b, c , etc., are experimentally determined constants. Then

$$\begin{aligned} H_{\text{per mol}} &= \int (a + bT + cT^2 + \dots) dT \\ &= aT + b\frac{T^2}{2} + c\frac{T^3}{3} + \dots + C^* \end{aligned}$$

In this way H for a constant-pressure process becomes a function of temperature and of experimentally determined constants a, b, c , etc. Likewise the heat of reaction, $H_{\text{products}} - H_{\text{reactants}} = \Delta H$, and the change in ΔH with temperature is also a function of temperature. Expressed otherwise, *the amount of heat flow that accompanies a given chemical reaction at constant pressure depends on the temperature at which the reaction takes place*.

We have already seen (page 92) that it is the free-energy change ΔF and not ΔH that is the criterion of chemical equilibrium. However, one of the most useful ways of determining ΔF is by means of an equation which involves ΔH .

By definition

$$F = E - TS + \frac{pV}{J}$$

But
$$E + \frac{pV}{J} = H$$

So by substitution

$$F = H - TS$$

If this equation is differentiated, we have

$$dF = dH - TdS - SdT$$

When this equation is applied to a reaction that takes place isothermally, $SdT = 0$, and the free-energy change of the reaction is given by the definite integral of $dH - TdS$, i.e.

$$\int_1^2 dF = F_2 - F_1 = \int_1^2 dH - \int_1^2 TdS$$

or
$$\Delta F = \Delta H - T \Delta S$$

In the first paragraph of this section we saw that ΔH at any temperature may be evaluated from specific heat data. In order to determine ΔS for the reaction $\Delta S = S_{\text{products}} - S_{\text{reactants}}$, we must know the absolute values of the entropies of each of the substances involved. Such knowl-

* The evaluation of the constant of integration C , the computation of heats of reaction and of change in heats of reaction with temperature are fully treated in G. N. Lewis and Merle Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw Hill, pp. 101 ff.

edge requires the determination of the constant of integration; i.e., at constant pressure

$$S = \int C_p \frac{dT}{T} = \int \frac{a + bT + cT^2 + \dots}{T} dT$$

$$= a \log_e T + bT + c \frac{T^2}{2} \dots + \text{const}$$

In order to evaluate the integration constant we must know the value of S at the boundary condition of T equal to absolute zero. Many experimenters, notably Nernst, Lewis, and Eucken, have investigated this problem. As a result of extensive research conducted by them and by others, a principle known as the Third Law of Thermodynamics has been formulated. Lewis and Randall* state this law as follows, in a way broad enough to permit its extension as experimental justification makes it possible to do so: "If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, *every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.*"

In accordance with the Third Law, the integration constant of the entropy equation for pure crystals is zero, thus making possible the computation of absolute entropies from specific heat data. This has been done and tables of absolute entropies of considerable extent have been prepared.† These data are widely used ‡ in conjunction with computed values of ΔH to determine ΔF . With knowledge of the value of ΔF for a certain temperature, it is possible to predict whether or not a reaction that would be industrially valuable is thermodynamically possible at that temperature. Further, a series of such computations made for different temperatures determines the temperature range within which the reaction is possible and so gives invaluable information concerning the operating conditions that must be maintained in order that the reaction may take place.

PROBLEMS

1. What is implied by the term reversibility? What are the conditions of complete reversibility? Describe a process which could be reversible.
2. In any frictional process, what is the immediate destination of the work energy expended to overcome friction? Discuss fluid friction and mechanical friction.

* *Ibid.*, p. 448.

† *International Critical Tables*, edited for the National Research Council by Edward W. Washburn *et al.*, McGraw-Hill.

‡ C. G. Maier, *Zinc Smelting from a Chemical and Thermodynamic Viewpoint*, Bureau of Mines, Bull. 324 (1930); R. S. Dean, *Use of Thermodynamical Data to Study the Chemical Reactions of Metallurgical Processes*, Bureau of Mines, Information Circular 6395 (1930).

- 3 Draw a diagram of the Carnot cycle on a pV plane. Describe each process taking place around the cycle. State how and when heat flows. State when work is done and whether it is done on or by the medium.
- 4 Discuss the *significance* of the Carnot cycle for the study of thermodynamics. What is wanted is a *critical, thoughtful* evaluation of what the cycle means and the ideas to which it leads.
- 5 Explain how an isothermal change can take place when there must be a temperature difference to bring about heat flow.
- 6 State and discuss fully the significance of the three characteristics of the Carnot cycle, known collectively as the Carnot Principle, which make it the most efficient cycle for the transformation of heat into work.
- 7 Define unavailable energy, available energy, finite source, infinite source.
- 8 Discuss the influence of temperature of addition of heat and temperature of rejection of heat on the efficiency of heat utilizing cycles.
- 9 The inventor of an oil engine claims for it a consumption of 0.31 lb of fuel (yielding 19,000 Btu per lb) per indicated hp-hr. The edges of a nickel test piece (mp 2660° F) just fuse in the cylinder of this engine and the exhaust temperature is 800° F. Test the probability of the correctness of the inventor's claim.
- 10 A Carnot engine which delivers 10 hp takes 120,000 Btu per hour from a source at 340° F. Find the receiver temperature. One hp-hr equals 2545 Btu.
- 11
 - a State the Second Law of Thermodynamics.
 - b Discuss the physical meaning of this law.
 - c What does the Second Law imply concerning the most effective condition for heat flow?
 - d What is your interpretation of the practical significance of the Second Law?
- 12 What is the concept of entropy? How is it defined and what is its use? For a reversible process, what is determined by the product of entropy change and condenser or refrigerator temperature, and by the product of entropy change and the temperature of the addition of heat?
- 13 Write the expression for efficiency of the Carnot cycle in terms of heat quantities of temperatures, and of areas. From the above expressions derive expressions for

(a) Available energy	
(b) Unavailable energy	Infinite source
(c) Entropy change	Infinite source
(d) Entropy change	Finite source
(e) Unavailable energy	Finite source
- 14
 - a Sketch the Carnot cycle on the pV and TS diagrams and describe fully the physical significance of each line.
 - b Identify the areas which represent heat absorbed, heat rejected, and heat transformed into work, and give a geometrical statement of Carnot efficiency.
 - c Under what conditions does area on a TS diagram represent heat quantity?

15. Relate reversibility and irreversibility to entropy change on isothermal and adiabatic processes. What area on a TS diagram represents increase of unavailable energy for an irreversible adiabatic change? What area on a TS diagram represents heat added on a reversible process?
16. Discuss the relationship between entropy change and heat flow. Why is the entropy change zero in an adiabatic frictionless process? What is the effect of fluid friction on the entropy change of a system? How do unavailable and available energy vary with the entropy change of a system? How do available energy and unavailable energy of a system vary with a change in T_R (lowest available temperature)?
17. Compute the entropy change for 10 lb of air when heated reversibly at constant volume from 60°F to 200°F . C_v for air = 0.17 Btu per lb.
18. Heat is added to 10 lb of a medium whose specific heat (for the process) is 0.20 Btu per lb per $^\circ\text{F}$, raising the temperature from 60°F to 260°F . The medium is used in a cycle which rejects heat to a cold body at a constant temperature of 50°F . (a) How much heat was added? (b) What was the entropy change of the medium accompanying the addition of heat? (c) How much of this heat was unavailable? (d) How much of this heat was available? (e) Represent the process by a sketch on a TS diagram and indicate areas that represent heat added, available energy, and unavailable energy.
19. In a mercury boiler the mercury is heated from 300°F to 680°F and is then vaporized at constant pressure. After passing through a turbine the mercury condenses at 250°F . Compute (a) the heat added per pound of mercury, (b) the available energy per pound of mercury.
Specific heat of Hg = 0.032
Latent heat of vaporization of Hg at 680°F = 90 Btu per lb
20. Five lb of water at 70°F enter a boiler and are heated to the boiling point, 382°F . The heat required to evaporate the water at this temperature is 842 Btu per lb. (a) What is the total change in entropy of the water in going from the state at which it enters the boiler to complete vapor? (b) What is the total heat added to bring about this change? (c) If the lowest available condenser temperature is 70°F , how many foot-pounds of work could be obtained theoretically from the heat added? (d) What effect does an increase in entropy during a reversible process have on (1) available energy, (2) unavailable energy?
21. In a certain steam cycle, the entropy change resulting from warming and evaporating water in the boiler is 1.8 entropy units per pound of steam. The condenser operates at a temperature of 92°F and measurements show that in the condenser 1160 Btu are rejected per pound of steam. What is the degree of reversibility of the cycle?
22. What physical condition causes the following? (a) External mechanical irreversibility, (b) internal mechanical irreversibility, (c) external thermal irreversibility, (d) internal thermal irreversibility.
23. Twenty lb of water at 180°F are mixed with 50 lb of water at 70°F . The lowest available receiver temperature is 35°F . (a) Compute the amount of heat energy that flowed from the hot to the cold water. (b) Compute

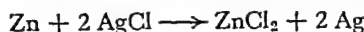
- the entropy of this energy as it departed from the hot water (c) Determine the entropy of the *same* amount of energy if withdrawn from the mixture (d) Is the availability of this energy greater or less as a result of the irreversible mixing? By how many Btu?
- 24 A ball (10 lb) of aluminum (sp ht 0.226) at a temperature of 700° F is dropped into a vessel containing 40 lb of water at 60° F. What is the final temperature obtained, and what is the net overall change in entropy of the system made up of the aluminum and the water?
- 25 A ball of copper weighs 5 lb and is at a temperature of 650° F. It is plunged into a vessel that contains 25 lb of water at 70° F. If the specific heat of copper is 0.093 and that of water is 1.00, find (a) the equilibrium temperature of the mixture, (b) the overall change of entropy of the copper-water system, (c) the change in availability of the heat that flowed with respect to a receiver at 40° F.
- 26 One lb of water at a pressure of 165 lb per sq in. is heated from 60° F to 366° F and then completely vaporized, the latent heat for that pressure being 857 Btu per lb. (a) Compute the total entropy change. (b) Compute the total heat added. (c) Compute the unavailable part of the total heat with reference to a 60° F condenser. (d) Represent the process by a sketch on a TS diagram and identify areas that represent heat added, available energy, and unavailable energy.
- 27 With the data in Problem 26, assume that the water was heated and vaporized by energy supplied by radiation from a furnace in which the temperature was 2500° F. (a) What was the entropy of the energy delivered by the furnace? (b) What was its unavailable energy with respect to a 60° F condenser? (c) What was the increase of entropy by reason of the irreversible heat transmission? (d) What was the corresponding increase in unavailable energy (60° F condenser)? (e) Interpret the meaning of the results.
- 28 a Does knowledge of the entropy of heat energy imply any information as to the extent to which the energy is available? If so, state the general relationship of entropy to availability.
b Does an irreversible heat flow cause an increase or decrease in entropy?
c From your answers to (a) and (b), what conclusions can you draw as to the effect of irreversible processes on the efficiency of thermodynamic cycles?
- 29 In a certain thermodynamic cycle 1 lb of the medium (sp ht 1 Btu/lb/°F) receives 500 Btu of heat while undergoing a change of temperature from 60° F to 560° F, and then receives an additional 650 Btu of heat isothermally and reversibly at 540° F. The medium is then expanded *irreversibly* through an engine, during which process the *entropy increases* 0.2 Btu per degree per lb. The engine exhausts at a temperature of 60° F. Compute the unavailable energy rejected per pound of medium. What is the thermodynamic efficiency of the cycle?
- 30 Total energy (enthalpy) is given by the expression $H = E + \frac{pV}{J}$. Show that, for a constant pressure change, change in total energy (dH) equals the change in heat (δQ).

31. State in detail the meaning of the terms heat of reaction, maximum work, free energy. Relate maximum work and free energy.
32. Using an electrolytic cell as an example, give the physical and chemical meaning of the definitions of the functions W_{\max} and F .
33. Discuss free energy from the following points of view: (a) definition, (b) determination, (c) meaning, (d) use.
34. What are the necessary and sufficient conditions with respect to free-energy change of a reaction in order that (a) it may take place spontaneously, (b) it may not take place spontaneously, (c) equilibrium exists?
35. Suppose that you are interested in determining the conditions under which a given process may occur spontaneously. How would you proceed?
36. State the conditions under which the path functions Q and W may be evaluated from the point functions intrinsic energy, total energy, W_{\max} , free energy. In each case give the reason for your answer.
37. a. What is the object of defining and discussing W_{\max} and F in a course in introductory thermodynamics?
b. The Gibbs-Helmholtz Equation is

$$-\Delta H = \frac{n96,500}{4.18} \left[\varepsilon - T \left(\frac{\partial \varepsilon}{\partial T} \right)_p \right]$$

From it and the definitions of ΔH and ΔF , show that the term $\frac{n96,500}{T} T \left(\frac{\partial \varepsilon}{\partial T} \right)_p$ represents heat added or rejected as a reaction proceeds isothermally and reversibly.

- c. If an electrolytic cell has a positive temperature coefficient, does it heat up or cool off in operation?
- d. For such a cell, is $-\Delta H$ larger or smaller than $-\Delta F$? Why?
38. a. Explain why $-\Delta F = \frac{nF\varepsilon}{4.18}$ measures the free energy of a chemical reaction.
b. From the Gibbs-Helmholtz Equation and (a), show what factor accounts for the difference between ΔH and ΔF and interpret it physically.
39. When this reaction, $C + CO_2 = CO$ (at $25^\circ C$), takes place, $\Delta F = +29,240$ cal. May the reaction take place spontaneously? Why?
40. The reduction of CdO by CO (at $25^\circ C$) is given by $CdO + CO = Cd + CO_2$. $\Delta F = +11,931$ cal while at $900^\circ K$, $\Delta F = -3857$ cal. What do these values of ΔF signify, and how may the information be used industrially?
41. In an electrolytic cell Zn , $ZnCl_2$, $AgCl$, Ag , the reaction is:



At $0^\circ C$, $\varepsilon = 1.015$ volts and $\frac{\partial \varepsilon}{\partial T} = -0.000402$. Compute $-\Delta H$ and $-\Delta F$ for this reaction at $0^\circ C$.

42. The voltage of the cell $Pb, Pb(C_2H_3O_2)_2 Cu(C_2H_3O_2)_2$ (sat), Cu , at $0^\circ C$ is 0.4764 . The rate of change of voltage with temperature is $+0.000385$.
(a) Determine the heat of the reaction at $0^\circ C$. (b) Determine the free

energy of the reaction at 0°C . (c) Which of these terms is a measure of the chemical affinity? (d) How do you account physically for the difference between $-\Delta H$ and $-\Delta F$?

43. In the electrolytic cell $\text{Cd}, \text{CdCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O} (\text{sat}) \text{AgCl}, \text{Ag}$, the reaction is $\text{Cd} + 2 \text{AgCl} \longrightarrow \text{CdCl}_2 + 2 \text{Ag}$. At 25°C ; $\mathcal{E} = 0.67531$ and $\frac{\partial \mathcal{E}}{\partial T} = -0.00065 \text{ v}/^\circ \text{K}$. Compute $-\Delta H$ and $-\Delta F$ for this reaction at 25°C .

Thermodynamic Properties of Gases; Gaseous Change of State

Introduction

In the preceding chapters we have been concerned almost wholly with the energy relationships that characterize thermodynamics. It was, however, pointed out in the beginning (page 5) that a material substance, or *working medium*, is always involved in energy transformation. Until now detailed consideration of the properties of any particular medium has been avoided, in order that the fundamental principles of energy transformation might not be obscured. With these principles clearly in mind, our next logical step is to study their application to various classes of media. Naturally, the study should start with that medium or class of media having the simplest possible behavior, a requirement which is satisfied by the so-called "permanent gases" — hydrogen, helium, oxygen, nitrogen, and air. Their designation as "permanent" had its origin at the time when it was thought that they could be neither liquefied nor solidified. Subsequent investigation has proved that this idea was incorrect, for it is now known that under suitable conditions of pressure and temperature, all known gases can be liquefied. Consequently the term "permanent" is now a misnomer, although it is still used to designate a gas of simple molecular structure which is liquefied only with difficulty.

Boyle's Law

Because of its relative simplicity, the behavior of a gas upon change of its state was one of the first thermodynamic phenomena to be studied quantitatively. In 1662 Robert Boyle published the results of his work on the changes in the volume of a mass of air kept at a constant temperature when the pressure was varied. Within about a 1% error, Boyle found that, *with the temperature constant*, volume varies inversely with pressure, i.e.

$$V \propto \frac{1}{p} \quad \text{or} \quad V = \frac{\text{const}}{p}$$

From this it follows that for the *isothermal change of a gas which behaves in accordance with Boyle's Law*

$$pV = \text{const} \quad \text{or} \quad p_1V_1 = p_2V_2 = p_3V_3, \text{ etc}$$

where the subscripts refer to the pressure and volume in a given state. This is a form of the expression pV^n for which $n = 1$.

It has been found that the deviation of the behavior of a gas from Boyle's Law depends on the nature of the gas studied, because measurements upon gases of simple molecular structure, like hydrogen and helium, show much less deviation from the law than do gases whose molecules have a more complicated structure. In accordance with these observations, there has been developed the abstract concept of a *perfect gas*, a gas that behaves *exactly* in accordance with Boyle's Law. The idea is a useful one, for the hypothetical behavior of a perfect gas provides a standard from which the deviations of real gases can be measured. If the deviation is not great, Boyle's Law may be used to advantage in making computations to a degree of accuracy adequate for engineering work.

The deviation of the behavior of real gases from that given by Boyle's Law has also been found to depend on the constant temperature at which the measurements are made. In general, the deviation increases as the conditions for condensation are approached. Therefore, the law may be applied with but small error to the behavior of the "permanent" gases which, under ordinary conditions, are at temperatures far above that at which they condense into the liquid phase. On the other hand, it *cannot* be applied to the behavior of vapors like steam. Not only is the molecular structure of such substances more complicated than that of simple gases, but also, under ordinary conditions, steam is relatively dense and is at a temperature near that of boiling water, i.e., the temperature of liquefaction of the vapor.

Charles' or Gay Lussac's Law

Another early investigation of gaseous behavior involved the determination of the way in which volume varied with the temperature when the pressure was held constant. In terms of the concept of absolute temperature, the experimental results of Charles and Gay-Lussac, known as Charles' or Gay-Lussac's Law, may be expressed by the equation

$$V \propto T \quad \text{or} \quad V = kT$$

where k is a factor of proportionality. If subscripts are used to identify the coordinates of two different states

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

This relationship has the same limitation as Boyle's Law, in that it applies *exactly only to the behavior of a perfect gas*. However, if the gas studied is of simple structure and is at a relatively low pressure (up to 10 atm) and at a temperature well above its boiling point, the error resulting from the application of Charles' Law will not exceed 2%.

Ideal Gas Law

The laws of Boyle and Charles may be combined into a single relationship, as follows :

$$V \propto \frac{1}{p} \text{ when } T \text{ is constant}$$

$$V \propto T \text{ when } p \text{ is constant}$$

When both temperature and pressure vary, the relationship which determines the variation of V must be

$$V \propto \frac{T}{p}$$

In equation form this relation becomes

$$V = \text{const} \times \frac{T}{p}$$

or $pV = \text{const} \times T$

or $\frac{pV}{T} = \text{const} = \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} = \dots$

Let the constant be designated as R . Then the equation $pV = RT$ describes the state of a perfect gas, i.e., a gas which behaves exactly in accordance with the Laws of Boyle and Charles. This equation is called the perfect or Ideal Gas Law. It will be helpful to interpret it in terms of graphic analysis. Since

$$T = \frac{pV}{R}$$

the equation is in the mathematical form of $z = f(x, y)$, which will be recognized as the equation of a surface. The surface represented by $pV = RT$ is shown in Fig. 4-1. Evidently, if the temperature is constant, the trace of the plane $T = \text{const}$ on this surface is the equilateral hyperbola $pV = \text{const}$. This equation has already been identified as that which characterizes the isothermal change of state of a perfect gas. It is worth noting (Fig. 4-2a) that as the temperature is decreased, the value of the constant $pV = \text{const}$ becomes less. Consequently an isothermal on the pV plane close to the origin may be recognized as one at relatively low temperature.

In a similar way, the curve which represents an isopiestic change of a perfect gas is the trace which the plane $p = \text{const}$ makes with the surface. Fig 4-2b shows that this is a straight line, inclined to both the T and V axes. Therefore, in a constant-pressure change with

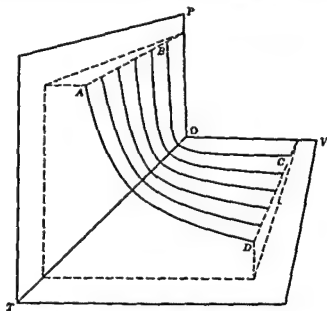


FIG. 4-1 Surface Represented by the Equation $pV = RT$

increasing volume, temperature increases, and conversely. This relationship is apt to be overlooked when the constant pressure curve is projected on the pV plane where it is foreshortened into a straight line parallel to the V axis (Fig 4-2c). Likewise consider the curve on the surface which represents an isometric change of a perfect gas. It is the trace made on the surface by the plane $V = \text{const}$, and is inclined to both the p and T axes (Fig 4-2d). This curve, like the isopiestic curve, is considerably foreshortened in projection upon the pV plane, where it appears as a straight line parallel to the p axis (Fig 4-2e). But again, examination of the curve on the surface itself shows that, in such a change, as the pressure decreases, the temperature must decrease, and conversely. The student will profit by keeping his attention on the actual nature of the various types of change as shown on the surface, rather than on the projections made on a particular plane like the pV plane.

The expression $pV = RT$ is the functional relation $T = \psi(p, V)$ which characterizes the behavior of a perfect gas. As such, and in conformity with the definition given on page 9, it is the *characteristic*

equation of a perfect gas. Its graphic representation may therefore be conveniently designated as the *characteristic surface*.

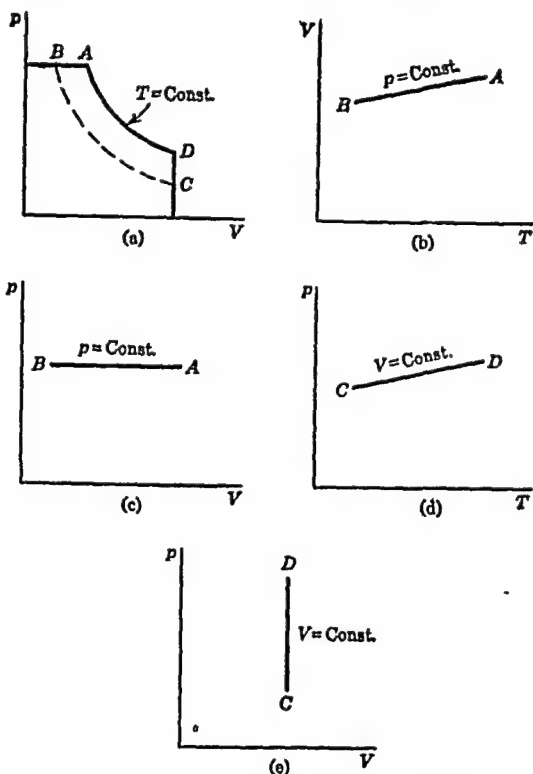


FIG. 4-2. Representation of Several Types of Changes of State for a Perfect Gas.

If the Ideal Gas Law is applied to a gas in two different states denoted by subscripts 1 and 2, there results

$$p_1 V_1 = RT_1$$

and

$$p_2 V_2 = RT_2$$

If the first of these equations is divided by the second, the result is

$$\frac{p_1 V_1}{p_2 V_2} = \frac{RT_1}{RT_2} \quad \text{or} \quad \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

an alternative expression of the law which is frequently very useful.

If the change from state 1 to 2 is carried out at constant volume

$$V_1 = V_2$$

and

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \quad \text{or} \quad \frac{p_1}{T_1} = \frac{p_2}{T_2}$$

This shows that at constant volume the pressure of an ideal gas varies directly with the absolute temperature. By Charles' Law the volume also varies directly with the absolute temperature. Theoretically, the change in pressure per unit change in temperature (pressure coefficient β) of an ideal gas should be the same as the volume coefficient α . That is

$$\alpha = \beta = \frac{1}{T} = 0.00366$$

The following measurements on hydrogen and air show how closely this condition is approached:

	α	β
Hydrogen	0.0036613	0.0036678
Air	0.0037099	0.0036871

Constant-Volume Gas Thermometer

The direct proportionality between the pressure of a gas and its absolute temperature finds a valuable application in the constant-volume gas thermometer, which was mentioned on page 7. With

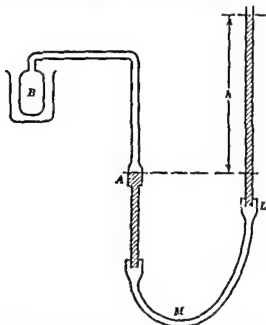


FIG. 4-3 Schematic Diagram of the Constant Volume Gas Thermometer.

hydrogen as the gas, this thermometer is the one selected by the International Bureau of Weights and Measures as a standard. As shown in the schematic diagram (Fig 4-3), the thermometer consists of a bulb *B*, which is filled with hydrogen and is connected by a small tube to a

mercury manometer M , of which the U -part is flexible tubing. At the point where the manometer joins the tube leading from the bulb, there is a small marker A . Because of the flexibility of the long arm LM of the U , the mercury can be made to rise until it just touches the mark at A , and so the volume of gas in the bulb and connecting tube down to A can be kept always the same. As the gas in the bulb is warmed, its pressure increases; hence, with rising temperature, greater pressure is required to keep the mercury up to A . The measurement of the required increase in pressure is the height h of the mercury column in L above mark A . It is the pressure exerted by this mercury column that maintains a constant level in the short arm of the U -tube. The absolute temperature T_2 corresponding to any pressure p_2 (as determined by measurement of the height h) is then determined from knowledge of the pressure p_1 corresponding to some reference temperature T_1 , such as the temperature of melting ice, 0°C or 273°K . With known values of p_1 , T_1 , and p_2 , simple substitution in $\frac{p_1}{T_1} = \frac{p_2}{T_2}$ makes it easy to solve for T_2 .

Units

When the gas law is expressed in the homogeneous form $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$, it is only necessary that the corresponding values of pressure, volume, and absolute temperature be expressed in the same units. Thus if p_1 is in lb per sq in., p_2 is in lb per sq in.; if V_1 is in cu ft, V_2 is in cu ft; and if T_1 is $^\circ\text{K}$, T_2 is $^\circ\text{K}$. Hence problems involving corresponding states of a gas may be readily solved, as illustrated by the following example.

Example

A mass of helium occupies a volume of 6.5 cu ft at a temperature of 50°F and a pressure of 14.7 lb per sq in. What volume does it occupy at a pressure of 6 lb per sq in. and a temperature of -60°F ?

Solution

$$\begin{array}{ll}
 p_1 = 14.7 \text{ lb per sq in.} & p_2 = 6 \text{ lb per sq in.} \\
 V_1 = 6.5 \text{ cu ft} & V_2 = ? \\
 T_1 = 50^\circ\text{F} = 460 + 50 & T_2 = -60^\circ\text{F} = 460 - 60 \\
 = 510^\circ\text{R} & = 400^\circ\text{R}
 \end{array}$$

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

$$\frac{14.7 \times 6.5}{510} = \frac{6 V_2}{400}$$

$$V_2 = \frac{400 \times 14.7 \times 6.5}{6 \times 510}$$

$$= 12.5 \text{ cu ft}$$

When a problem involves the determination of an unknown coordinate for a *single state of a gas* by the application of the law $pV = RT$, more attention must be paid to the units involved. In the British system of units, pressures are conventionally measured in lb per sq in., volumes in cu ft, and temperature in $^{\circ}\text{F}$. From the preceding discussion it is clear that the temperature used in the gas law must be converted to the absolute scale ($^{\circ}\text{Rankine}$) by the addition of 460° . Also, the *pressure should be converted into lb per sq ft* by multiplying by 144 in order that the product pV may have recognizable dimensions. When this is done, the dimensions of the product pV are those of work or energy, thus, $\text{lb per ft}^2 \times \text{ft}^3 = \text{ft lbs}$. Since the volume V is the volume of the gas present, the dimensions of the constant R must be in foot pounds per amount of gas present per degree. The dimensions of the equation $pV = RT$ give an added physical significance to temperature in that they show that *absolute temperature is a measure of the energy of a gas*.

The Gas Constant

In order to determine the value of R , an arbitrary and reproducible set of conditions is specified. Since R is constant, the value thus determined is valid for other states of the gas. The standard pressure is taken as 14.7 lb per sq in. or 2116.8 lb per sq ft, which may be considered as normal atmospheric pressure. The standard temperature is taken as 32°F or 492°R . If one pound of the gas is considered, v represents the *specific volume, or volume per pound*. The following tabulation gives values for v of the simple gases under standard conditions of pressure and temperature.

	v
Hydrogen	177.9 cu ft per lb
Oxygen	11.21 cu ft per lb
Nitrogen	12.8 cu ft per lb
Air	12.39 cu ft per lb

When one pound of gas is considered, the gas constant R is denoted by B . Consequently, by direct substitution of the values of p , v , and T under standard conditions, the gas constant per pound for oxygen is

$$B = \frac{pv}{T} = \frac{14.7 \times 144 \times 11.21}{492} = 48.3 \text{ ft lb per lb per } ^{\circ}\text{R}$$

By Avogadro's Law, equal volumes of gases under the same conditions contain the same number of molecules, and so the masses of such volumes are to each other as their molecular weights. This leads at once to the definition of the mol, a unit of weight of particular usefulness in dealing

with gases. A mol is the weight represented by the molecular weight expressed in units of weight. Since the molecular weight of oxygen is 32, a gram-mol of oxygen is 32 g, and a pound-mol of oxygen is 32 lb. By Avogadro's Law, the volume per mol of different gases is the same under the same conditions of pressure and temperature. In the cgs system of units the standard gram-molal volume is 22.4 liters; in the British system of units the standard pound-molal volume is 358.7 cu ft.

The gas constant is denoted by R when the unit of weight is the mol. Since the volume of a mol of any gas is the same under the same conditions, the value of R is the same for all gases. Because of this fact, R is frequently called the Universal Gas Constant. Its value is obtained thus

$$14.7 \times 144 \times 358.7 = R \times 492$$

$$R = 1544 \text{ ft-lb per lb-mol per } ^\circ R$$

With energy expressed in heat units, this is

$$R = \frac{1544}{778} = 2 \text{ (approx) Btu per lb-mol per } ^\circ R$$

Because the unit of heat is defined in terms of weight and temperature, R in heat units per mol per degree is a pure number and is independent of the system of units employed. This is illustrated by conversion of each of the units Btu, pound-mol, and degrees R to the corresponding cgs values.

$$1 \text{ Btu} = 252 \text{ cal}$$

$$1 \text{ lb-mol} = 454 \text{ g-mol}$$

$$1^\circ R = \frac{5}{9}^\circ K$$

$$\text{Thus } R = 2 \times \frac{252}{1} \times \frac{454}{1} \times \frac{5}{9} = 2 \text{ (approx) cal per g-mol per } ^\circ K$$

Since the molal volume V is the molecular weight m times the specific volume v , the molal gas constant R is m times B , the gas constant per pound; i.e., $R = mB$. This provides a way of determining B from the molecular weight and the universal value of R . For example, since the molecular weight of oxygen is 32, B for oxygen is

$$B = \frac{1544}{32} = 48.3 \text{ ft-lb per lb per } ^\circ R$$

Application of the Ideal Gas Law

The Ideal Gas Law may be applied to n units of quantity of the gas by multiplying both sides of the equation by n , the number of units of quantity present. Then, when the quantity is expressed in pounds, where pounds is designated by M ,

$$pMv = MBT$$

If V is used to denote the volume of M lb, this becomes

$$pV = MBT$$

Likewise, if n mols of the gas are considered

$$pno = nRT$$

and again if V represents the volume of n mols, this becomes

$$pV = nRT$$

The following example illustrates the use of the equation

Example

Compute the pounds of oxygen which can be stored in a 5 cu ft container at a pressure of 300 lb per sq in abs and a temperature of 60° F?

Solution

$$p = 300 \text{ lb per sq in} = 300 \times 144 \text{ lb per sq ft}$$

$$= 43,200 \text{ lb per sq ft}$$

$$V = 5 \text{ cu ft}$$

$$T = 60 + 460 = 520^\circ \text{ R}$$

$$B = 48.3 \text{ ft lb per lb per } ^\circ \text{ R}$$

By substitution

$$43,200 \times 5 = M \times 48.3 \times 520$$

$$M = 8.6 \text{ lb}$$

The method of attack is the same if the unknown quantity is pressure, volume, or temperature

Other Characteristic Equations

It must be kept in mind that the *characteristic equation of a perfect gas is only a useful approximation to the behavior of a real gas*. The approximation grows closer as the gas becomes more rarefied. Conversely, the deviation increases as the gas grows denser. Because of their mobility and other physical properties, gases and vapors have wide application as the working substance in thermodynamic cycles and processes. Hence it is a matter of considerable importance to determine characteristic equations of gases and vapors with the greatest possible accuracy. One of the best known analytic derivations of a characteristic equation for real gases was made by van der Waals. By an approach based on the kinetic theory of gases, he deduced that in addition to the external pressure on a gas, there is also an internal pressure, set up by the mutual attracting forces between the molecules, which is inversely proportional to the square of the volume. Moreover, he considered in his equation the volume of the molecules themselves, which of course constitutes a space in which molecular motion is not possible. The van der Waals characteristic equation is

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

Values for the constants a and b , which may be determined in several ways,* are given for a few common gases in Table 4-1.

TABLE 4-1. CONSTANTS FOR VAN DER WAALS' EQUATION †

	a	b
Air	1.33×10^6	36.6
Ammonia	4.16×10^6	37.3
Carbon dioxide	3.6×10^6	42.8
Methane	2.25×10^6	42.8
Sulphur dioxide	6.8×10^6	57.2

The units for these constants are: pressure in atmospheres, volume in cc per gram-mol, and temperature in degrees Kelvin. With these units, the Universal Gas Constant has the value of 82.06 cc atm per g-mol per °K.

As with the Ideal Gas Law, the van der Waals Equation may be applied to n units of quantity (in this case gram-mols) by multiplying both sides by n ; thus

$$\left(p + \frac{a}{v^2}\right)(vn - nb) = nRT$$

And again, if V is taken as the volume of n mols, $V = vn$, and

$$\left(p + \frac{a}{V^2/n^2}\right)(V - nb) = \left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

In solving problems by means of van der Waals' Equation, it is best to carry out the solution in the units in which the constants are given. The conversion of the given data to these units can be done much more readily than can the conversion of the equation itself.

Example

Compute the pressure of 1 lb of sulphur dioxide occupying 0.5 cu ft at a temperature of 20° C.

Solution

$$1 \text{ lb of SO}_2 = 454 \text{ g} \quad \text{or} \quad \frac{454}{64} = 7.09 \text{ g-mols}$$

$$\therefore n = 7.09$$

$$V = 0.5 \text{ cu ft} = 0.5 \times 28.3 \times 10^3 \text{ cc} = 14.15 \times 10^3 \text{ cc}$$

$$T = 20 + 273 = 293^\circ \text{ K}$$

$$a = 6.8 \times 10^6$$

$$b = 57.2$$

$$R = 82.06$$

* Saha and Srivistava, *A Textbook of Heat*, India Press, pp. 164-167.

† Computed from critical data from *International Critical Tables*.

By substitution in the van der Waals Equation

$$\left(p + \frac{7.09^2 \times 6.8 \times 10^6}{(14.15 \times 10^3)^2}\right)(14.15 \times 10^3 - 7.09 \times 57.2) = 7.09 \times 82.06 \times 293$$

$$p = \frac{170,300}{13,745} - \frac{342 \times 10^6}{200 \times 10^6} = 12.4 - 1.71 = 10.69 \text{ atm}$$

$$= 157 \text{ lb per sq in. abs}$$

Had the problem been solved by the Ideal Gas Law, the calculated pressure would have been, with British units throughout

$$p = \frac{1 \times 24.14 \times (68 + 460)}{0.5 \times 144} = 177 \text{ lb per sq in.}$$

an error of nearly 13%.

When either V or n is unknown, the solution becomes algebraically complicated and is best made by graphic methods.*

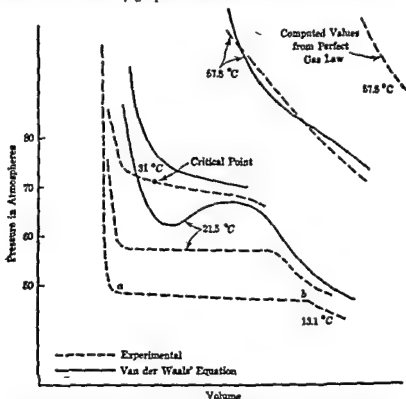


FIG. 4-4. Isotherms of CO_2 , Showing Deviation from van der Waals' Equation (Reprinted by permission from *Industrial Chemical Calculations*, by Hougen and Watson, published by John Wiley & Sons, Inc.)

Although van der Waals' Equation is today the best means of determining the behavior of gases at high pressure, it is not an entirely accurate representation of the facts. The solid lines in the graph in Fig. 4-4 are isotherms obtained by plotting van der Waals' Equation

* See O. A. Hougen and K. M. Watson, *Industrial Chemical Calculations*, Wiley, pp 55-56.

for carbon dioxide on the pV plane. The dotted lines represent the experimental results of Andrews (1869) on the same substance. The deviation is considerable, especially in the region ab , which is where the gas liquefies. This discrepancy, which looks serious, can be explained by correct interpretation of the theoretical curve, but the deviation in the gaseous region cannot be so easily accounted for. The inadequacy of the van der Waals Equation accurately to represent the experimental facts has caused numerous investigators to set up other characteristic gas equations, most of which are empirical in nature. Their use is usually complicated by the large number of empirically determined constants introduced to make the equation fit the facts. Some of the better known of these equations are:

$$\text{Clausius} \quad p = \frac{RT}{v - b} - \frac{c}{T(v + a)^2}$$

$$\text{Dieterici} \quad p = \frac{RT^{-\frac{a}{RTc}}}{v - b^e}$$

$$\text{Lees} \quad p = \frac{RT}{v - b} - \frac{ap^{\frac{1}{3}}}{Tv^{\frac{2}{3}}}$$

Callendar (for steam)

$$v = \frac{RT}{p} + b - \frac{c}{T^n}$$

Beattie-Bridgman

$$pv^2 = RT \left[v + B_0 \left(1 - \frac{b}{v} \right) \right] \left(1 - \frac{c}{vT^3} \right) - A_0 \left(1 - \frac{a}{v} \right)$$

The Beattie-Bridgman Equation, although complicated, is of significance in that its five constants may be evaluated rather simply from a relatively small amount of experimental data.

Critical Pressure, Volume, and Temperature

The graph of the results of Andrews' experiments shown in Fig. 4-4 merits further attention because it sheds considerable light on the behavior of matter as it changes phase, in this case from a gas to a liquid. If the isothermal of 13.1°C is traced from right to left, the pressure first increases as the volume decreases. From points b to a , however, the pressure remains constant and the volume continually decreases. This part of the curve represents the process of liquefaction; it is worth noting that *both pressure and temperature remain constant*. During this change, the carbon dioxide is present in both the gaseous and the liquid phases and the diminution in volume is accomplished by the progressive condensation of the gaseous portion until at point a the substance is all liquid.

In the same way, the temperature of water boiling at atmospheric pressure is constant at a value which depends upon the height of the barometer. The graph further shows that after liquefaction is reached, a decrease in volume can be accomplished only by a great increase of pressure. This fact is responsible for the common inaccurate statement that liquids are incompressible. A better conclusion is that liquids are only slightly compressible.

The graph shows that the isothermal for 21.5°C has much the same character as that for 13.1°C , except that the horizontal section is shorter. As isothermals for higher and higher temperatures are drawn, this section becomes progressively shorter until finally, in the isothermal for 31.4°C , it disappears. At this temperature and above, there is no transition process by which condensation takes place. Consequently, carbon dioxide cannot be liquefied by any pressure, however great, if the temperature is above 31.4°C . The point C at which condensation just ceases to be possible is called the *critical point*. The isothermal through this point is at the *critical temperature*, and the pressure and volume coordinates of the point are called the *critical pressure* and *critical volume*. Each substance has its own characteristic critical point, hence knowledge of the critical data — i.e., pressure, volume, and temperature, — of various substances is a matter of considerable importance in the technical use of the substance as a thermodynamic medium.

TABLE 4-2 CRITICAL PROPERTIES OF SOME COMMON SUBSTANCES*

	Critical Pressure p_c in Atm	Critical Volume v_c for 1 g mol	Critical Temperature t_c in $^{\circ}\text{C}$
Air	37.2		-140.7
Ammonia	111.5	72.4	132.4
Carbon dioxide	73	95.5	31.1
Methane	45.8	99	-82.5
Sulphur dioxide	77.7	123	157.2
Water	217.7	45	374

The above discussion shows that it is impossible to liquefy any substance by pressure alone if it is above its critical temperature. Moreover, if the substance is cooled to a temperature slightly below the critical, there is no necessity for using a pressure greater than the critical pressure. It was lack of knowledge of these facts that made it impossible for early experimenters to liquefy the common gases like hydrogen, nitrogen, and oxygen, even though tremendous pressures were used. It is now clear

* Data reproduced from *International Critical Tables*

that their unsuccessful results were caused not by the "permanent" gaseous nature of the substance, but by the fact that they attempted the liquefaction at temperatures considerably above the low critical temperatures of these substances.

Compressibility Factors

The characteristic equations for gases, other than $pV = nRT$, are not in a form that permits quick and easy calculation. Furthermore, the Perfect Gas Law may *not* be used to describe the behavior of real gases under the extreme conditions of pressure and temperature prevalent in industry today. A way out of this difficulty is provided by the use of empirical constants, called *compressibility factors*, as correction factors for the Perfect Gas Law Equation. For example, by the equation $p\bar{v} = BT$, the volume per pound of nitrogen at 1000 lb per sq in. abs and -70°F is

$$\begin{aligned} \bar{v} &= \frac{BT}{p} & B \text{ for nitrogen} &= \frac{1544}{28} \\ &= \frac{55.14 \times (460 - 70)}{1000 \times 144} & &= 55.14 \text{ ft-lb per lb per } ^\circ\text{R} \\ &= 0.1495 \text{ cu ft per lb} \end{aligned}$$

Experiment gives this value as 0.1316 cu ft per lb, a value which is only 88% of that calculated. The error is too great to be neglected. The equation can be made to yield the correct value if the right-hand side is multiplied by 0.88, i.e., $p\bar{v} = 0.88 BT$. The factor 0.88 is called the *compressibility factor for nitrogen in the state specified*. The empirical adaptation of the Perfect Gas Law is therefore

$$\begin{aligned} pV &= CMBT \\ \text{or} \quad pV &= CnRT \end{aligned}$$

the form of the equation depending on whether the units of weight are pounds or mols. In either case C is the compressibility factor for the gas in the particular state considered. The compressibility factor is a function of pressure, temperature, and the nature of the gas and so its value varies with different gases and different states. Compressibility factors may be used in the homogeneous form of the Perfect Gas Law as applied to two different states *provided the proper factor is used with each state*. Thus

$$\begin{aligned} p_1V_1 &= C_1nBT_1 \\ p_2V_2 &= C_2nBT_2 \end{aligned}$$

If the first equation is divided by the second

$$\frac{p_1V_1}{p_2V_2} = \frac{C_1T_1}{C_2T_2} \quad \text{or} \quad \frac{p_1V_1}{C_1T_1} = \frac{p_2V_2}{C_2T_2}$$

The usefulness of the compressibility factor is clearly dependent on the ability to determine the value of the factor for a particular substance and state. As the result of extensive experimental work, compressibility data are available over a wide range of temperature and pressure for

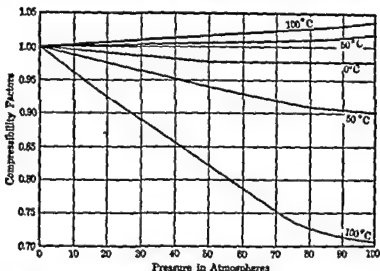


FIG. 4-5 Compressibility Factors of Nitrogen Corresponding to Specified Pressures and Temperatures (Reprinted by permission from *Industrial Chemical Calculations* by Hougen and Watson published by John Wiley & Sons Inc.)

most of the gases used industrially. These data have been collected and expressed in graphic form* in order to provide a convenient means of determining the factor for any desired pressure or temperature. As an illustration, one such graph for nitrogen is shown in Fig. 4-5.

Variable Specific Heats of Gases

In many problems dealing with gaseous media it is necessary to know the values of the specific heats c_p and c_v over wide ranges of temperature and pressure. This is particularly true of the combustion process in an internal combustion engine in which the temperature range is several thousand degrees. As mentioned in Chapter 1 (page 15) specific heat generally is a function of temperature. Also at high pressures and low temperatures, the instantaneous value of c_p depends upon both temperature and pressure.

The general variation of the molal specific heat with temperature is expressed by the equation

$$C = a + bt + ct^2 +$$

*O. A. Hougen and K. M. Watson, *Industrial Chemical Calculations*, Wiley, pp. 59-60.

in which t is the temperature and a , b , and c are constants determined by experiment. The latest and most accurate equations of this form, applicable to various common gases, have been worked out by Eastman* from experimental data and are as follows:

Units:	C_p in Btu per lb-mol per °F: t in °F
$N_2, O_2, CO, NO, HCl, HI, HBr, F_2$	$C_p = 6.923 + 0.000373 t + 0.40 \times 10^{-7} t^2$
H_2, HF	$C_p = 6.937 + 0.000218 t + 0.68 \times 10^{-7} t^2$
H_2O	$C_p = 8.346 + 0.000465 t + 0.414 \times 10^{-8} t^2$
NH_3	$C_p = 8.308 + 0.0035 t$
CO_2, SO_2	$C_p = 9.000 + 0.0027 t - 0.256 \times 10^{-8} t^2$
CH_4	$C_p = 8.33 + 0.0053 t$
Monatomic gases and metallic vapors	$C = 4.98$

At this point it is well to consider the steps by which an expression for specific heat in terms of one temperature scale may be transformed into the comparable expression on another temperature scale. A specific example will serve this purpose.

For temperatures between 300 and 2500° K, Eastman gives the following equation for the specific heat of hydrogen in calories per gram-mol per degree, with t in *degrees Kelvin*.

$$C_p = 6.85 + 0.28 \times 10^{-3} t + 0.22 \times 10^{-6} t^2$$

Then, for example, at 1000° K

$$C_p(1000^\circ \text{K}) = (6.85 + 0.28 + 0.22) = 7.35 \text{ cal per g-mol per } ^\circ \text{K}$$

In order to obtain an expression that is valid when t is in *degrees centigrade*, we must substitute

$$t = t_c + 273$$

Then $C_p = 6.85 + [0.28 \times 10^{-3}(t_c + 273)] + [0.22 \times 10^{-6}(t_c + 273)^2]$

$$C_p = 6.85 + 0.28 \times 10^{-3} t_c + 0.28 \times 10^{-3} \times 273 + 0.22 \times 10^{-6} t_c^2 + 0.22 \times 10^{-6} \times 2 \times 273 t_c + 0.22 \times 10^{-6} (273)^2$$

$$C_p = 6.9428 + 0.4 \times 10^{-3} t_c + 0.22 \times 10^{-6} t_c^2$$

As a check let us compute C_p for the same temperature as before.

$$1000^\circ \text{K} = 727^\circ \text{C}$$

* E. D. Eastman, *Specific Heat of Gases*, Bureau of Mines, Technical Paper No. 445 (1929).

When this value of t_e is substituted in the preceding equation

$$C_p(727^\circ \text{C}) = 6.9428 + 0.4 \times 10^{-3} \times 727 + 0.22 \times 10^{-6} \times (727)^2 \\ = 7.3498 \text{ cal per gram mol per } ^\circ \text{C}$$

The slight discrepancy between this figure and that previously obtained results from failure to carry the computation to the final decimal point.

To transform the equation to one in terms of degrees Fahrenheit we substitute

$$t_e = \frac{5}{9}(t_f - 32) \text{ in}$$

$$C_p = 6.9428 + 0.4 \times 10^{-3} t_e + 0.22 \times 10^{-6} \times t_e^2$$

$$\text{Then } C_p = 6.9428 + 0.4 \times 10^{-3} (t_f - 32) \frac{5}{9} + 0.22 \times 10^{-6} \times [(t_f - 32) \frac{5}{9}]^2$$

$$C_p = 6.9428 + 0.4 \times 10^{-3} \times \frac{5}{9} t_f - 0.4 \times 10^{-3} \times 32 \times \frac{5}{9} \\ + 0.22 \times 10^{-6} \times \frac{25}{81} \times t_f^2 - 0.22 \times 10^{-6} \times 2 \\ \times 32 \times \frac{25}{81} \times t_f + 0.22 \times 10^{-6} \times (32)^2 \times \frac{25}{81} \\ \equiv 6.9428 + 0.222 \times 10^{-3} t_f - 0.00711 + 0.679 \times 10^{-7} t_f^2 \\ - 0.004 \times 10^{-3} t_f + 0.00007$$

$$C_p = 6.9358 + 0.000218 t_f + 0.679 \times 10^{-7} t_f^2$$

Let us use the same temperature as before to check this equation

$$1000^\circ \text{K} = 1340.6^\circ \text{F}$$

$$C_p(1340.6^\circ \text{F}) = 6.9358 + 0.000218 \times 1340.6 + 0.679 \times 10^{-7} \\ \times (1340.6)^2 \\ = 7.3505 \text{ Btu per lb-mol per } ^\circ \text{F}$$

Similarly, an equation valid for t in degrees Rankine may be obtained by substituting

$$t_f = t_R - 460$$

in the equation expressed in terms of degrees Fahrenheit

The value of C_p for each of these gases is readily obtained from that of C_p by consideration of the physical distinction between C_p and C_v . As previously described, C_p is larger than C_v by the amount of energy required to provide space for the medium against the constant pressure acting. The measure of the difference may be obtained by differentiating the Non Flow Energy Equation thus

At constant volume

$$\delta Q = dE + 0 \text{ (in heat units)}$$

If this is expressed as a partial derivative with respect to T

$$\left(\frac{\delta Q}{\partial T}\right)_v = \left(\frac{\partial E}{\partial T}\right)_v$$

Since $\left(\frac{\delta Q}{\partial T}\right)_v = C_v$ the specific heat at constant volume is measured by the rate of change of intrinsic energy with temperature

At constant pressure

$$\delta Q = dE + p dV \text{ (in heat units)}$$

Let this also be expressed as a partial derivative with respect to T , pressure of course being the variable held constant. Then

$$\left(\frac{\delta Q}{\delta T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p$$

In order to evaluate this equation, $\left(\frac{\partial V}{\partial T}\right)_p$ must be determined for the particular medium under consideration. This is done by taking the indicated partial derivative of its characteristic equation. Since most of the gases in the preceding table follow the Perfect Gas Law reasonably well, we shall use it as the characteristic equation. Also, in order to be consistent with the units of the table we shall use the form in which the unit of quantity is the pound-mol. The indicated partial derivative is obtained thus

$$pV = RT$$

$$p \left(\frac{\partial V}{\partial T}\right)_p = R \left(\frac{\partial T}{\partial T}\right)_p = R$$

or

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$$

When this value is substituted in the original equation

$$C_p = \left(\frac{\partial E}{\partial T}\right)_p + p \frac{R}{p}$$

It will be shown presently that for a perfect gas intrinsic energy is a function of temperature only. Therefore it is immaterial whether p or V is held constant, and so

$$\left(\frac{\partial E}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_v = C_v$$

Then, by substitution

$$C_p = C_v + R$$

When the Gas Law is in units of pound-mols the value of R in heat units is closely equal to 2 Btu per lb-mol per °R. Consequently, Eastman's equations for C_p per pound-mol may be transformed into equations for C_v per pound-mol by subtracting 2 from the constant term of each.

The equations may also be readily transformed into expressions for c_p and c_v , *specific heats per pound of medium*, by dividing each term by the molecular weight.

For example, if the medium is N_2

$$c_p = \frac{6.923}{28} + \frac{0.000373}{28} t + \frac{0.40 \times 10^{-7} t^2}{28} \text{ Btu per lb per } ^\circ\text{F}$$

$$c_v = \frac{4.923}{28} + \frac{0.000373}{28} t + \frac{0.40 \times 10^{-7} t^2}{28} \text{ Btu per lb per } ^\circ\text{F}$$

and for HCl

$$c_p = \frac{6.923}{36.5} + \frac{0.000373}{36.5} t + \frac{0.40 \times 10^{-7} t^2}{36.5} \text{ Btu per lb per } ^\circ\text{F}$$

$$c_v = \frac{4.923}{36.5} + \frac{0.000373}{36.5} t + \frac{0.40 \times 10^{-7} t^2}{36.5} \text{ Btu per lb per } ^\circ\text{F}$$

The variation of C_p with pressure results from the fact that at high pressures the average intermolecular distance is considerably reduced. Consequently, the attractive force between molecules is increased and relatively more energy is required to produce the molecular agitation characteristic of an increase of temperature. The effect is most marked

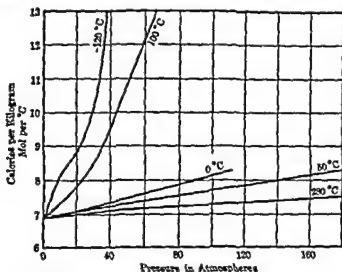


FIG. 4-6 Effect of Pressure upon the Instantaneous Molar Heat Capacity of Air at Constant Pressure (Reprinted by permission from *Industrial Chemical Calculations* by Hougen and Watson published by John Wiley & Sons Inc.)

when the high pressure is accompanied by low temperature. This is precisely the same condition that produces enhanced deviation from the Perfect Gas Law, and for the same reason. As a result, the variation of C_p with pressure may be neglected when the behavior of a gas is approximately represented by the Perfect Gas Law. When its behavior is no longer capable of being described by that law, the variation of C_p with pressure may not be ignored. The curves shown in Fig. 4-6 indicate that the

variation of C_p with pressure is not great at high temperatures, even when the pressure is extremely high. But when even a moderately high pressure is accompanied by low temperature, the variation is decidedly large.

The student must give particular attention to the use of the variable specific heat equations. Because constant specific heats are generally used in the elementary study of heat, it is a common error to use the equations to determine an arithmetical average value of c_p or c_v which is then treated as a constant. This procedure can be valid only *when the equation is linear* in character. In all other cases, the equation *must be integrated with respect to t between the designated limits of temperature* in order to determine quantity of heat.

Thus, since

$$\left(\frac{\delta Q}{dt}\right)_p = C_p = \text{molal specific heat at constant pressure}$$

$$\delta Q = C_p dt$$

$$\text{and } {}_1Q_2 = \int_{t_1}^{t_2} C_p dt$$

Similarly, if the medium is heated at constant volume

$${}_1Q_2 = \int_{t_1}^{t_2} C_v dt$$

Example

How much heat is required to raise the temperature of 1 lb-mol of nitrogen from 100° F to 3000° F at constant volume?

Solution

$$\begin{aligned} {}_1Q_2 &= \int_{t_1}^{t_2} C_v dt \\ C_v \text{ for } N_2 &= (6.923 - 2) + 0.000373 t + 0.40 \times 10^{-7} t^2 \\ \therefore {}_1Q_2 &= \int_{100}^{3000} (4.923 + 0.000373 t + 0.40 \times 10^{-7} t^2) dt \\ &= 4.923 t + 0.000373 \frac{t^2}{2} + 0.40 \times 10^{-7} \frac{t^3}{3} \Big|_{100}^{3000} \\ &= 4.923(3000 - 100) + \frac{0.000373}{2} (3000^2 - 100^2) \\ &\quad + \frac{0.40 \times 10^{-7}}{3} (3000^3 - 100^3) \\ &= 14,276.7 + 1676.6 + 360 \\ &= 16,313.3 \text{ Btu} \end{aligned}$$

The heat required per pound is readily obtained by dividing by 28, the molecular weight of nitrogen.

$${}_1q_2 = \frac{16,313.3}{28} = 582.6 \text{ Btu per lb}$$

From 32° F to 392° F the value of c_p per pound of nitrogen is given * as constant at 0.173. If this value is used in the example, the result is

$$1q_2 = 0.173(3000 - 100) = 517.3 \text{ Btu per lb}$$

* This result is slightly over 11% in error when compared with the more accurate value obtained by using Eastman's Equation

Gaseous Mixtures

In industrial processes and cycles, the thermodynamic medium is more often a mixture of several gases than a single one. For example, in an internal combustion engine the expansive medium which pushes the piston down is a mixture of the products of combustion. These usually include nitrogen, carbon dioxide, carbon monoxide, and water vapor. In order to deal adequately with problems involving mixtures of this nature, a means must be provided for determining the specific heat and gas constant of the mixture. Both of these quantities depend upon weight. Consequently, their average values for a gaseous mixture depend upon the *weight composition* of the mixture. The analysis of gaseous mixtures is usually reported in terms of *volume composition* and so the first step in determining the properties of a gaseous mixture is the conversion of volume composition to weight composition.

Again Avogadro's Law may be invoked to advantage. By this law, a mol of any gas under defined conditions contains the same number of molecules. Also the molal volume under standard conditions is the same for all gases. A mol of a mixture, therefore, has the same volume as a mol of any of its constituents. If analysis reveals that a certain mixture contains 9% hydrogen by volume, a mol of the mixture contains 0.09 mol of hydrogen. Since the weight of a mol of hydrogen is simply its molecular weight, it is a simple matter to determine the weight of hydrogen per mol of mixture. The sum of the weights of all of the constituents determined in this way is the weight of a mol of the mixture. The weight composition is then easily determined by dividing the weight of each component by the weight of the whole. This procedure is illustrated in the following example.

Example

A certain producer gas has the following composition by volume

H ₂	15%
CO	22%
CH ₄	3%
CO ₂	9%
N ₂	51%

What is its weight composition?

* C. D. Hodgman and N. A. Lange, *Handbook of Chemistry and Physics*, Chemical Rubber Co.

Solution

	vol fract = mol fract		mol wt		wt in lb	wt fract
H ₂	0.15	×	2	=	0.3	0.012
CO	0.22	×	28	=	6.16	0.245
CH ₄	0.03	×	16	=	0.48	0.019
CO ₂	0.09	×	44	=	3.96	0.158
N ₂	0.51	×	28	=	14.28	0.567
					25.18 lb	1.001
					Weight per mol of mixture	

While it is not possible for a mixture to have a true molecular weight, its weight per mol may be used as an *apparent* molecular weight for the determination of its specific heat and gas constant. Thus, in the preceding example, the apparent molecular weight of the mixture is 25.18 lb.

The gas constant per pound of mixture is then obtained by dividing the Universal Gas Constant per mol by the apparent molecular weight.

$$B_{\text{mixture}} = \frac{1544}{25.18} = 61.32 \text{ ft-lb per lb per } ^\circ \text{R}$$

The gas constant per pound may also be obtained from the weight composition. By Dalton's Law of Partial Pressures, the sum of the pressures of the constituents of a mixture of gases is equal to the total pressure exerted by the mixture, i.e.

$$p_1 + p_2 + p_3 \cdots = p_{\text{mixture}}$$

Since each constituent occupies the entire volume and is at the temperature of the mixture, the Perfect Gas Law for each component is

$$p_1 = \frac{M_1 B_1 T}{V} \quad p_2 = \frac{M_2 B_2 T}{V} \quad p_3 = \frac{M_3 B_3 T}{V} \quad \text{etc.}$$

in which M_1, M_2, M_3 give the weight in pounds of each component, and B_1, B_2 , and B_3 are the respective gas constants per pound of the components. Then

$$p_{\text{mixture}} = \frac{T}{V} (M_1 B_1 + M_2 B_2 + M_3 B_3 \cdots)$$

If M is the weight of the entire mixture in pounds, the Perfect Gas Law for it is

$$pV = MB_{\text{mixture}}T$$

or
$$p_{\text{mixture}} = \frac{MT}{V} (B_{\text{mixture}})$$

Comparison of the two equations for p_{mixture} at once yields the fact that

$$MB_{\text{mixture}} \frac{T}{V} = \frac{T}{V} (M_1B_1 + M_2B_2 + M_3B_3 + \dots) = \Sigma M_iB_i$$

or $B_{\text{mixture}} = \frac{\Sigma M_iB_i}{M}$

Since $M = \Sigma M_i$

Then $B_{\text{mixture}} = \frac{\Sigma M_iB_i}{\Sigma M_i}$

In the case where M_1, M_2, M_3 , etc., indicate weight per cent, their sum is of course equal to 100, hence under such circumstances

$$B_{\text{mixture}} = \Sigma M_iB_i$$

Given the data in the preceding example, the gas constant B of the producer gas is determined by this method in the following way

	wt fract (M_i)	gas const per lb (B)	M_iB
H ₂	0.012	772.0	9.26
CO	0.245	55.14	13.51
CH ₄	0.019	96.31	1.83
CO ₂	0.158	35.09	5.54
N ₂	0.567	55.10	31.24
$B = \Sigma M_iB_i =$			61.38

Specific Heat of Gaseous Mixtures

The definition of specific heat in terms of unit weight of substance makes possible the determination of the average specific heat of a mixture. The process by which this is done is the same as that outlined in the preceding paragraph for the determination of the gas constant B for a mixture. That is, the sum of the products formed by multiplying the weight of each component by its specific heat is equal to the total weight of the mixture times the average specific heat. In equation form, with C_1, C_2, C_3 , etc., denoting specific heat per mol of the respective components, and n_1, n_2, n_3 , etc., the weight in mols of each component present, the relation is

$$n_1C_1 + n_2C_2 + n_3C_3 + \dots = (n_1 + n_2 + n_3)C_{\text{mixture}}$$

It is convenient to take n_1, n_2, n_3 , etc., as the mol per cent of each component which is, of course, the same as the volume percentage composition. Their sum is then 1 mol of the mixture.

Example

Find the variable specific heat at a constant volume per mol and per pound of the producer gas mentioned in the example on page 126. For convenience, the volume composition is repeated.

H ₂ ,	15%
CO,	22%
CH ₄ ,	3%
CO ₂ ,	9%
N ₂ ,	51%

Solution

Eastman's Equation for N₂ and CO are the same. They may therefore be grouped together.

	mol %		C _v
H ₂	0.15.....	4.937 + 0.000218 t + 0.68	× 10 ⁻⁷ t ²
CO, N ₂	0.73.....	4.923 + 0.000373 t + 0.40	× 10 ⁻⁷ t ²
CH ₄	0.03.....	6.33 + 0.0053 t	
CO ₂	0.09.....	7.00 + 0.0027 t	+ 0.256 × 10 ⁻⁶ t ²
	mol % × C _v		
H ₂	0.7406 + 0.000033 t + 0.102	× 10 ⁻⁷ t ²	
CO, N ₂	3.5938 + 0.000273 t + 0.29	× 10 ⁻⁷ t ²	
CH ₄	0.1899 + 0.00016 t		
CO ₂	0.63 + 0.000243 t - 0.23	× 10 ⁻⁷ t ²	
C _v mixture =	5.1543 + 0.000709 t + 0.162	× 10 ⁻⁷ t ²	
per mol			

From an earlier example, the apparent molecular weight of the producer gas is 25.18. Therefore, c_v per pound for this gas is

$$C_v = \frac{5.1543}{25.18} + \frac{0.000709 t}{25.18} + \frac{0.162 \times 10^{-7} t^2}{25.18}$$

$$= 0.244 + 0.00028 t + 0.00643 \times 10^{-7} t^2$$

Joule's Law

There is one more property of gases that must be discussed before we are ready to undertake the study of what happens when a gas changes state. This property is intrinsic energy, which on pages 41-42 was shown to be a point function and hence dependent on the coordinates. What we need to know now is: For a perfect gas, what is the precise nature of the dependence of intrinsic energy on the coordinates? This question was raised early in the nineteenth century and both Gay-Lussac and Joule independently investigated the matter experimentally. Joule used an apparatus, represented in Fig. 4-7, in which a quantity of air was confined in a vessel *A* at high pressure and at the same temperature as that of the surrounding water bath *W*. The stopcock *S* was then opened and the air allowed to rush into the evacuated vessel *B*. The

temperature in A fell as a result of the expansion and consequent decrease in intrinsic energy. In B , the temperature increased because of the progressive compression. But when pressure equilibrium was established between A and B , the temperature of the water bath, which measured the temperature of the system as a whole, was found to be inappreciably different from its initial value. Joule concluded that there

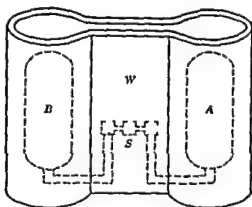


FIG 4-7 Apparatus for Joule's Experiment

had been no heat flow to or from the confined air, i.e., ${}_1Q_2$ for the change was zero. Also, since the volume of the two vessels as a whole did not change, no effect on the surroundings resulted and so ${}_1W_2$ was also zero. Therefore, by the Non-Flow Equation, ${}_1Q_2 = \Delta E + {}_1W_2$, ΔE was also zero, and the experiment showed that the intrinsic energy of the air was the same whether it occupied both of the vessels or only one of them. In short, the intrinsic energy of the air was independent of volume as well as pressure. More refined experiments subsequent to Joule's have shown that for real gases there is a slight dependence of intrinsic energy upon volume which his apparatus was not sensitive enough to detect. However, strict thermodynamic reasoning shows that Joule's result is to be expected of a gas that obeys the Laws of Boyle and Charles, i.e., a perfect gas.

By its nature, intrinsic energy is a function of the coordinates, i.e., $E = f(t, v)$. In Joule's experiment both intrinsic energy and temperature remained constant, while the volume increased very considerably. Therefore, the important deduction can be made that *for a perfect gas, intrinsic energy depends only on the temperature*. This result is known as Joule's Law. Since temperature is the manifestation of molecular motion, all of the intrinsic energy of a gas which follows Joule's Law must be in the kinetic form. Further, because molecular motion ceases only

at absolute zero, intrinsic energy must be a function of absolute temperature, i.e., $E = f(T)$.

Joule-Thomson Effect

As we have seen before, the behavior of real gases deviates from that of a perfect gas and the deviation becomes more marked in the measure that conditions for liquefaction are approached. It is under such conditions that intermolecular forces (page 24) play an important role in determining the behavior of a gas. What happens is that the amount of intrinsic energy in the potential form increases as intermolecular distances decrease. The quantitative measure of this effect is determined by a refinement of Joule's apparatus with which he and Thomson made a long series of experiments in the period from 1852 to 1862. The object of the experiment was to make accurate determination of the temperature of a gas before and after its free expansion through a porous plug. Because of the importance of the plug to the apparatus, the experiment is often known as the Porous Plug Experiment. The term "free expansion" means that no external mechanical work is done by the expanding gas. However, consideration must be given to pV , the flow-work term, for the expanded gas certainly must provide space for itself during the expansion.

The arrangement of the apparatus used by Joule and Thomson is represented schematically in Fig. 4-8. Gas at a known uniform temperature and pressure is admitted to one end of a tube in which is

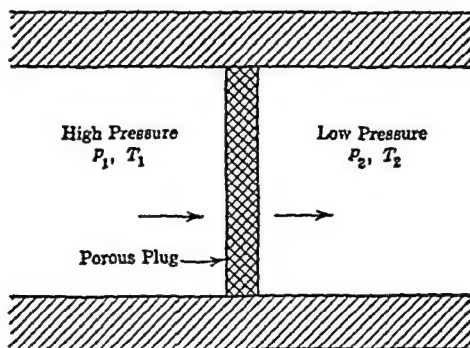


FIG. 4-8.

placed a porous plug P . The gas finds its way through the plug to the region of lower pressure on the other side, where its temperature and pressure are again accurately measured. The whole apparatus is carefully insulated so that the process is adiabatic and ${}_1Q_2 = 0$. Because

the expansion is free, ${}_1W_2$ is zero, and the fluid friction can be considered zero. No chemical changes are involved and the velocity of the gas on both sides of the plug is the same. Also there is no change in elevation. Consequently, the General Energy Equation for the process per pound of medium is

$$\frac{u_1^2}{2g} + p_1V_1 + z_1 + e_1 + c_1 + J_1q_1]_{-0} = \frac{u_2^2}{2g} + p_2V_2 + z_2 + e_2 + c_2 + J_2q_2]_{-0} + {}_1W_2]_{-0}$$

$$e_1 + p_1V_1 = e_2 + p_2V_2 \quad (\text{in work units})$$

Since enthalpy h is defined as $e + \frac{pV}{J}$, this may be further reduced to the simple statement

$$h_1 = h_2 \quad (\text{in heat units})$$

This result shows that in the Joule Thomson experiment it is *enthalpy*, rather than intrinsic energy, that remains constant. If p_1V_1 is not equal to p_2V_2 , there is a change in intrinsic energy. It would be natural to expect that this in turn would result in a change in temperature. The expectation is realized by the experimental measurements of Joule and Thomson and of others who have worked with similar apparatus. With only two exceptions, these measurements establish the fact that under ordinary conditions and whatever the nature of the gas the temperature in state 2 is *less* than that in state 1. However, the free expansion of hydrogen from 4.7 to 1.00 atmosphere at 10° C results in a *slight increase* of temperature. Under approximately the same conditions of expansion helium also exhibits a similar heating effect. The phenomenon of temperature change upon free expansion is known as the Joule-Thomson effect and its quantitative measure, $\left(\frac{\partial t}{\partial p}\right)_h$, is called the Joule-Thomson

coefficient. In practice, the effect occurs whenever a medium is allowed to go from a region of high pressure to one of low pressure without performing external mechanical work. For example, if one is operating a steam engine, he may control the speed by the throttle valve. The more the valve is closed, the greater is the pressure drop through it. This is an exceedingly wasteful method of regulation, inasmuch as free expansion is a highly irreversible process and so results in a decided increase in entropy. Because the practical manifestation of the Joule-Thomson effect is so closely associated with the action of a throttle valve, free expansion is often called a throttling process. The term "wire-drawing process" is also used to denote the same type of change.

The explanation of the Joule-Thomson effect depends upon the

constancy of enthalpy during adiabatic free expansion. Enthalpy is the sum of the intrinsic energy and the product pV , and for real gases these two factors do *not* depend upon the pressure in the same way. Of course, for a perfect gas, Joule's Law shows that E depends *only* on temperature and so the change in E with pressure is zero. Also, Boyle's Law requires that the product pV depend *only* on temperature. Its variation with pressure must therefore also be zero in the ideal case. Consequently, a perfect gas would not exhibit any Joule-Thomson effect. But for real gases the change of intrinsic energy with decrease in pressure always produces a cooling effect. The change in pV with a pressure drop may cause either a heating or a cooling effect in a real gas, depending upon the conditions of pressure and temperature (see Fig. 4-5). Since these two effects may be of different sign or different magnitude or both, the observed Joule-Thomson effect may be either heating, cooling, or, in the limiting case, entirely non-existent. For any given gas there is a temperature, called the *temperature of inversion*, at which the effects resulting from a change in E and in pV cancel each other and the Joule-Thomson coefficient is zero. Below its temperature of inversion, a gas is cooled by free expansion. Above that temperature, a heating effect results. Certain inversion temperatures have been experimentally determined and have been found to agree reasonably well with the values predicted by the theory. Olzewski found the temperature of inversion for hydrogen to be -80.5°C . Below that temperature and in accord with the theory, hydrogen exhibited the same cooling effect upon free expansion as that shown by other gases at room temperatures. The inversion temperature for helium has been observed to be -233°C . Hence it is not surprising that at room temperature helium exhibits a heating effect when permitted to expand freely.

Linde Process for the Liquefaction of Gases

The Joule-Thomson effect is applied practically in the Linde process for the liquefaction of gases. The industrial uses of liquefied gases have increased enormously in the last two decades and the preparation of such liquids has now become a major technical industry. In the Linde process (Fig. 4-9), gas is compressed to a high pressure (e.g., 200 atm) and is then passed through a cooling device C fitted with a coil of pipe through which water is circulated. Heat is abstracted from the gas in this apparatus and its temperature is thereby reduced. The pressure remains high, however, as the stream of gas flows along the pipe to an expansion valve E , through which it expands freely to a region of low pressure (approximately 50 atm). If the temperature of the gas at this

point is below its inversion temperature, the Joule Thomson effect causes the expansion to be accompanied by a sharp drop in temperature. The cooled gas then flows back to the compressor intake in an annular space surrounding the pipe through which it was delivered to the valve.

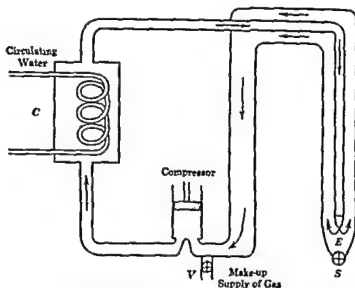


FIG 4-9 Arrangement of Apparatus of the Linde Process for Liquefaction of Air

Because of its low temperature, the expanded gas absorbs heat from the stream of high pressure gas which it surrounds until an equilibrium temperature is reached. The low pressure gas then returns to the compressor, where it is again compressed and the cycle is repeated. The abstraction of heat from the high pressure stream of gas results in a lowering of its temperature even before its expansion. Consequently, when in its turn it passes through the expansion valve, the temperature drop of the Joule Thomson effect results in the achievement of a definitely lower temperature than before. As the gas goes round and round through this cycle, the temperature at the exit from the expansion valve becomes progressively lower. Eventually it reaches the temperature of liquefaction corresponding to the pressure existing on the low pressure side of the valve. When this point is reached a fraction of the gas expanded through the valve is liquefied, the remainder, which is the larger part, returns to the compressor as before and serves to precool the gas about to be expanded. After liquefaction begins the amount of gas condensed represents a loss of medium so far as the events of the cycle are concerned. If this progressive loss were to continue, the com

pressor would soon fail to maintain its delivery pressure and this in turn would mean that the temperature of liquefaction could not be maintained. Consequently, additional gas, equal in amount to that condensed, is continuously pumped into the apparatus from the outside through the valve V . Under these conditions there is a steady output of liquefied gas which is drawn off through the stopcock S .

Gaseous Change of State

The object of the first three chapters of this book was to give a thorough understanding of the laws governing the transformation of heat energy. Up to now, the aim of the present chapter has been to present the characteristic properties of an important class of media, the gases. We are now ready to merge these two aims into the single one of determining ways of evaluating the amount of each of the several types of energy involved in the change of state of a gas. Naturally, any formula for such evaluation amounts to the application of a general principle to a specific case and so depends jointly on the laws of thermodynamics and on the characteristic properties of the medium. For the sake of simplifying the analysis as much as possible, we shall first make this application to non-flow processes. Also, we shall make it in terms of the five limiting changes of state most frequently encountered, i.e., constant-volume, constant-pressure, isothermal, adiabatic, and polytropic processes. Finally, we shall consider that the Perfect Gas Law is the characteristic equation of a real gas, meanwhile keeping clearly in mind the probable deviation of fact from this assumption.

Non-Flow Constant-Volume Change of State of a Perfect Gas

Each of the limiting types of change is conveniently described in terms of p and V by assigning the proper value to the exponent n in the equation $pV^n = \text{const.}$ For a constant-volume change, n must be such that the exponent of p becomes zero and that of V becomes 1. These conditions are met by taking the n th root of both sides of the equation, thus

$$p^{\frac{1}{n}}V = (\text{const})^{\frac{1}{n}} = K \text{ (another const)}$$

In order that the exponent of p shall be zero, n must be infinite. Thus

$$p^{\frac{1}{\infty}}V = K$$

$$p^0V = K$$

or

$$V = K$$

Consequently, a constant-volume change is characterized by the fact that $n = \infty$ in the equation $pV^n = \text{const.}$

A non flow constant volume change of state of any medium also has the characteristic that it results in *no external work* being done (see page 38) This conclusion is quickly established when it is considered that

$${}_1W_2 = \int_1^2 p dV$$

For a constant volume change dV equals zero, and so ${}_1W_2 = \int p dV$ also equals zero. As a necessary result, the Non Flow Energy Equation for such a change is

$$\begin{aligned} J_1Q_2 &= (E_2 - E_1) + {}_1W_2 = 0 \\ J_1Q_2 &= E_2 - E_1 \end{aligned}$$

From the definition of c_v , the heat added during a constant volume change is

$$J_1Q_2 = JM c_v (T_2 - T_1) \text{ in work units}$$

In this expression c_v is considered to be a constant and M is used to denote the number of pounds of gas involved in the change. By substitution in the preceding expression, it follows that for M lb of gas

$$E_2 - E_1 = \Delta E = JM c_v (T_2 - T_1)$$

It is worth pointing out that this equation is in strict accord with Joule's Law that the intrinsic energy of a perfect gas depends on the temperature.

Since it is assumed that the gas obeys the Perfect Gas Law, the equation for ΔE may be expressed in terms of p and V by use of the relationship $pV = MBT$. Thus

$$T_1 = \frac{p_1 V_1}{MB} \qquad T_2 = \frac{p_2 V_2}{MB}$$

$$\begin{aligned} \text{and} \quad E_2 - E_1 &= JM c_v \left(\frac{p_2 V_2}{MB} - \frac{p_1 V_1}{MB} \right) \\ &= \frac{JM c_v}{M} \frac{p_2 V_2 - p_1 V_1}{B} \end{aligned}$$

Since the difference of the molal specific heats C_p and $C_v = R = 2$ (approx) Btu per lb mol per $^{\circ}R$, the difference between c_p and c_v per pound is $\frac{R}{m} = \frac{B}{J}$ (m = molecular weight, B in work units per pound)

Therefore

$$c_p - c_v = \frac{B}{J} \quad \text{or} \quad B = J(c_p - c_v)$$

If this value for B is substituted in the expression for $E_2 - E_1$, there results

$$E_2 - E_1 = J c_v \left[\frac{p_2 V_2 - p_1 V_1}{J(c_p - c_v)} \right]$$

Dividing numerator and denominator by c_v

$$E_2 - E_1 = \frac{p_2 V_2 - p_1 V_1}{\frac{c_p}{c_v} - 1}$$

The ratio $\frac{c_p}{c_v}$ is widely used in the experimental study of specific heat. Indeed, it is more practicable to make accurate measurements of c_p and the ratio $\frac{c_p}{c_v}$ and then compute c_v than it is to measure c_v directly. Because of this and because of its frequent occurrence in thermodynamics generally, the ratio $\frac{c_p}{c_v}$ is conventionally designated by the single letter k , i.e.

$$k = \frac{c_p}{c_v}$$

With this simplification, the intrinsic energy equation in terms of p , V , and k is

$$E_2 - E_1 = \frac{p_2 V_2 - p_1 V_1}{k - 1}$$

Since intrinsic energy is a point function, its change $\Delta E = E_2 - E_1$ is quite independent of the path over which the change is made. This is shown in Fig. 4-10. Because E of a perfect gas is a function of temperature only,

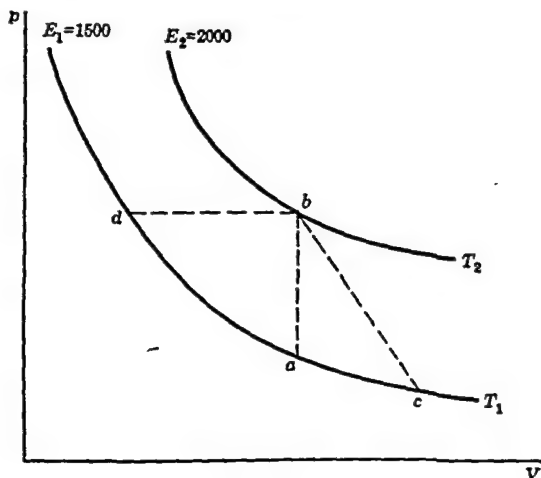


FIG. 4-10.

the value of E is the same at any state point on the isothermal T_1 . Suppose that it has the constant value of $E_1 = 1500$ ft.-lb. Along the isothermal T_2 , the value of E is also constant, but because T_2 represents a

higher temperature than T_1 , its amount is greater than before. Suppose that for the state points on T_2 the value of E is constant at $E_2 = 2000$ ft lb. Then for each of the changes $d-b$, $c-b$, $a-b$ the change in intrinsic energy is exactly the same, e g

$$E_2 - E_1 = 2000 - 1500 = 500 \text{ ft lb}$$

Hence the type of change is of no importance in the determination of intrinsic energy change. From the point of view of obtaining a formula for ΔE of a perfect gas, the constant-volume change is much the easiest to study. Thus the above expression, although derived for a constant volume change, is valid for a non flow change of a perfect gas of any character whatsoever.

As a result of the foregoing analysis, the detailed application of the Non-Flow Energy Equation to the constant volume change of a perfect gas is

$$\underbrace{JM c_v (T_2 - T_1)}_{{}_1Q_2} = \underbrace{\frac{p_2 V_2 - p_1 V_1}{k - 1}}_{E_2 - E_1} + \underbrace{0}_{{}_1W_2}$$

The use of these relationships is illustrated by the following example.

Example

Three lb of nitrogen in a container at a pressure of 100 lb per sq in. abs and temperature of 60°F are heated at constant volume until the pressure is 250 lb per sq in. abs

$$c_p = 0.244 \quad c_v = 0.173$$

(a) What is the volume of the container? (b) What is the amount of heat added?

Solution

(a) The volume of the container may be determined from $pV = MBT$, in which

$$\begin{aligned} B &= \frac{1544}{\text{mol wt } N_2} = \frac{1544}{28} = 55.2 \text{ ft lb per lb per } ^\circ\text{R} \\ p &= 100 \text{ lb per sq in.} = 100 \times 144 \text{ lb per sq ft abs} \\ T &= 60 + 460 = 520^\circ\text{R} \\ M &= 3 \end{aligned}$$

By substitution of these values

$$V = \frac{3 \times 55.2 \times 520}{100 \times 144} = 5.97 \text{ cu ft}$$

(b) The amount of heat added may be computed in two ways. The first, which is easier, is to determine the final temperature T_2 from the relation

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

and substitute it and the initial temperature T_1 , together with the value of c_v , in the formula ${}_1Q_2 = Mc_v(T_2 - T_1)$

$$\frac{100}{520} = \frac{250}{T_2}; T_2 = 1300^\circ \text{R}$$

Then ${}_1Q_2 = 3 \times 0.173(1300 - 520) = 405 \text{ Btu}$

The second method of determining ${}_1Q_2$ is to determine the change in intrinsic energy from the expression

$$\Delta E = E_2 - E_1 = \frac{p_2 V_2 - p_1 V_1}{k - 1} \text{ (in work units)}$$

The result, when converted into heat units by dividing by J , is equal to ${}_1Q_2$ by the analysis given in the preceding paragraph.

$$p_2 = 250 \times 144 \text{ lb per sq ft abs}$$

$$p_1 = 100 \times 144 \text{ lb per sq ft abs}$$

$$V_2 = V_1 = 5.97 \text{ cu ft}$$

$$k = \frac{c_p}{c_v} = \frac{0.244}{0.173} = 1.41$$

$$\text{Hence } \Delta E = \frac{5.97(250 \times 144 - 100 \times 144)}{1.41 - 1}$$

$$= \frac{129,000}{0.41} = 315,000 \text{ ft-lb}$$

$$\text{or } {}_1Q_2 = \Delta E = \frac{315,000}{778} = 405 \text{ Btu as before}$$

All of the foregoing paragraph is essentially concerned with the application of the First Law of Thermodynamics to a constant-volume change. In our discussion of the Second Law, we emphasized the fact that, so far as computation is concerned, it is the entropy change of the medium which leads to definite information concerning maximum availability. Therefore, in order to complete our application of the general laws to a specific change of state of a particular medium, we must give the means for determining entropy change. For a *reversible* constant-volume change of a gas, this is readily computed from

$$dS = \frac{\delta Q}{T}$$

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{\delta Q}{T}$$

For a constant-volume change

$$\delta Q = Mc_v dT$$

$$\text{Therefore } \Delta S = \int_{T_1}^{T_2} \frac{Mc_v dT}{T}$$

and if c_v is constant

$$\Delta S = Mc_v \log_e \frac{T_2}{T_1}$$

From the Perfect Gas Law, if V is constant

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

So

$$\frac{T_2}{T_1} = \frac{p_2}{p_1}$$

Hence, the expression for ΔS may be given in terms of p_1 and p_2 , thus

$$\Delta S = Mc_s \log_e \frac{p_2}{p_1}$$

Non Flow Constant Pressure Change of State of a Perfect Gas

A constant pressure change is described very simply by the equation $p = \text{const}$. In order to reduce $pV^n = \text{const}$ to this form, the value of n must be zero. Thus

$$\begin{aligned} pV^0 &= \text{const} \\ p &= \text{const} \end{aligned}$$

Consequently, a constant pressure change is characterized by $n = 0$ in $pV^n = \text{const}$.

Let us now consider the evaluation of the terms of the Non Flow Energy Equation for a constant pressure change of state of a gas. In terms of the temperature change, the heat ${}_1Q_2$ added or abstracted is

$${}_1Q_2 = JMc_s(T_2 - T_1) \text{ (in work units)}$$

The intrinsic energy change is independent of the nature of the change and the formula for it is the same as for the constant volume change: i.e.

$$\Delta E = E_2 - E_1 = \frac{p_2V_2 - p_1V_1}{k - 1} \text{ (in work units)}$$

or, since by the conditions of the change $p_2 = p_1$

$$\Delta E = \frac{p(V_2 - V_1)}{k - 1}$$

In terms of temperature, ΔE is given by

$$\Delta E = JMc_v(T_2 - T_1)$$

The work done during an isopiestic change is represented graphically by the area on the pV plane under the straight line $p = \text{const}$. This area is seen at once to be equivalent to $p(V_2 - V_1)$, a result that is easily verified by evaluating the work function $\int_V^V p dV$ with p constant. Thus

$$\begin{aligned}
 {}_1W_2 &= \int_{v_1}^{v_2} p dV \\
 &= p \int_{v_1}^{v_2} dV \text{ when } p \text{ is constant} \\
 &= p(V_2 - V_1)
 \end{aligned}$$

Then, in terms of the coordinates, the Non-Flow Energy Equation for a constant-pressure change of a gas is

$$\underbrace{JMc_p(T_2 - T_1)}_{J_1Q_2} = \underbrace{\frac{p(V_2 - V_1)}{k - 1}}_{\Delta E} + \underbrace{p(V_2 - V_1)}_{{}_1W_2} \text{ (in work units)}$$

$$\text{or } JMc_p(T_2 - T_1) = JMc_v(T_2 - T_1) + p(V_2 - V_1)$$

It is to be noted by reference to Fig. 4-2 (page 109) that reduction of volume at a constant pressure results in decreased temperature. Therefore, for such a change, the value of T_2 in the above expression is less than that of T_1 . Consequently the term $JMc_p(T_2 - T_1)$ is minus. This means that the reduction of volume of a gas at constant pressure requires the abstraction of heat. Conversely, when volume is increased at constant pressure, heat must be added.

The temperature change during a non-flow constant-pressure process also indicates the nature of the intrinsic energy change. By reference to the expression for ΔE in terms of temperature

$$\Delta E = JMc_v(T_2 - T_1)$$

it follows at once that a constant-pressure reduction of volume results in a *decrease* in intrinsic energy, because for such a process T_2 is less than T_1 . The converse result naturally follows when the volume is increased at constant pressure.

These thoughts may be summarized by saying that when volume is reduced at constant pressure, the heat rejected is equivalent to the *sum* of the decrease in intrinsic energy and of the work done on the system. When volume is increased at constant pressure, heat must be supplied equivalent to the *sum* of the increase in intrinsic energy and the work done by the medium. Of course the latter statement is directly implied by the definition of c_p .

Example

Six lb of air are reduced in volume from 10.2 cu ft to 5.8 cu ft at a constant pressure of 130 lb per sq in. abs. (a) How much work must be done on the medium? (b) How much heat must be rejected?

Solution

$$M = 6 \text{ lb}$$

$$p_1 = p_2 = 130 \text{ lb per sq in. or } 130 \times 144 \text{ lb per sq ft abs}$$

$$V_1 = 10.2 \text{ cu ft}$$

$$V_2 = 5.8 \text{ cu ft}$$

$$T_1 = ?$$

$$T_2 = ?$$

$$B = 53.35 \text{ ft lb per lb per } ^\circ \text{R}$$

$$c_p = 0.24 \text{ Btu per lb per } ^\circ \text{F}$$

$$k = \frac{c_p}{c_v} = 1.4$$

(a) The work done in effecting the reduction in volume is given by ${}_1W_2 = p(V_2 - V_1)$ and this should be minus since work was done *on* the gas. Substitution of the given data gives

$$\begin{aligned} {}_1W_2 &= 130 \times 144(5.8 - 10.2) \\ &= -82,500 \text{ ft lb} \end{aligned}$$

(b) The heat abstracted during the process may be obtained in two ways. The easier method in this instance is to determine ΔE and combine it with ${}_1W_2$ to obtain ${}_1Q_2$, thus

$$\Delta E = \frac{p(V_2 - V_1)}{k - 1} = \frac{-82,500}{1.4 - 1} = -206,200 \text{ ft lb}$$

Then since ${}_1Q_2 = \Delta E + {}_1W_2$

the value of ${}_1Q_2$ for this process is

$$\begin{aligned} {}_1Q_2 &= \frac{\Delta E + {}_1W_2}{J} = \frac{-206,200 - 82,500}{778} \\ &= -371.5 \text{ Btu} \end{aligned}$$

The heat abstracted may also be found from the determination of T_1 and T_2 and substitution in

$$JM c_p (T_2 - T_1) = {}_1Q_2$$

Substitution of known values in $pV = MBT$ yields T_1 , thus

$$\begin{aligned} 130 \times 144 \times 10.2 &= 6 \times 53.35 \times T_1 \\ T_1 &= 598^\circ \text{R or } 138^\circ \text{F} \end{aligned}$$

The final temperature may be determined in the same way, but less arithmetic is involved if Charles' Law is applied

$$\begin{aligned} \frac{V_1}{V_2} &= \frac{T_1}{T_2} \\ \frac{10.2}{5.8} &= \frac{598}{T_2} \end{aligned}$$

$$T_2 = 339^\circ \text{R or } -121^\circ \text{F}$$

Then ${}_1Q_2 = 6 \times 0.24(339 - 598)$

$$= -372 \text{ Btu}$$

The agreement of this result with that previously obtained is well within the probable error in the data and the constants used.

The entropy change of a gas resulting from the flow of heat accompanying a *reversible* constant-pressure process is readily obtained from

$$dS = \frac{\delta Q}{T}$$

For a constant-pressure process $\delta Q = Mc_p dT$, and so

$$dS = \frac{Mc_p dT}{T}$$

If c_p is constant, this is easily integrated to obtain ΔS , thus

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{Mc_p dT}{T} = Mc_p \log_e \frac{T_2}{T_1}$$

Since by Charles' Law $\frac{T_2}{T_1} = \frac{V_2}{V_1}$ when p is constant, ΔS is also given by

$$\Delta S = Mc_p \log_e \frac{V_2}{V_1}$$

If c_p is variable and is given by an equation of the form

$$c_p = a + bT + cT^2$$

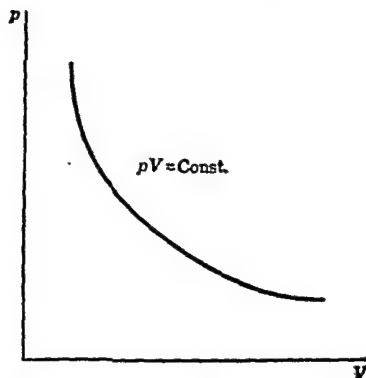
each term of the specific heat equation must of course be integrated with respect to T , i.e.

$$\begin{aligned} \Delta S &= M \int_{T_1}^{T_2} \frac{c_p dT}{T} = M \int_{T_1}^{T_2} \frac{(a + bT + cT^2)}{T} dT \\ &= M \left[a \left(\log_e \frac{T_2}{T_1} \right) + b(T_2 - T_1) + \frac{c}{2} (T_2^2 - T_1^2) \right] \end{aligned}$$

Non-Flow Isothermal Change of State of a Perfect Gas

It will be recalled that Boyle's Law for the pressure-volume relation of a perfect gas specified that the law is valid when the temperature remains constant. But this is precisely the condition that defines an isothermal change of state. Therefore, the equation in p and V which represents the isothermal change of state of a gas is $pV = \text{const}$ (Fig. 4-11). This expression may be obtained from $pV^n \equiv \text{const}$ if n is taken equal to 1; hence $n = 1$

may be said to characterize the isothermal change of a gas. The value $n = 1$ does not indicate an isothermal change of any other medium, for Boyle's



Isothermal Change for a Perfect Gas

FIG. 4-11.

Law is valid *only* for a perfect gas. In general, the equation of the isothermal change of any substance is determined by making the temperature term constant in the characteristic equation of that substance. Hence, for a gas of complicated structure or for a vapor, the pV equation for the isothermal change is not so simple as is that for a perfect gas, as may be readily appreciated from the complexity of the characteristic equations of such media.

In applying the Non-Flow Energy Equation to an isothermal change of a gas, there is immediate difficulty in evaluating ${}_1Q_2$. Since T is constant, the use of c_p or c_v , as in the two preceding types of change, has no meaning. There is a way out of this predicament, however, which is provided by the means available for evaluating the other terms of the equation. We shall therefore leave the question of evaluating ${}_1Q_2$ for a moment and consider the determination of ΔE and ${}_1W_2$.

By Joule's Law, the intrinsic energy change of a gas which follows the law $pV = nRT$ depends only on the absolute temperature. In the change now under consideration the medium is assumed to obey Joule's Law and the temperature is constant. Therefore, the stock of *intrinsic energy* is constant during the change, i.e., $\Delta E = 0$.

We already have deduced a formula for ${}_1W_2$ in terms of p and V for a change characterized by the value $n = 1$ in the equation $pV^n = \text{const}$ (pages 44–46). But this value of n is precisely the distinguishing feature of the pV equation for the isothermal change of a perfect gas. Consequently, the formula for ${}_1W_2$ previously obtained is directly applicable to the present case, that is

$${}_1W_2 = p_1V_1 \log_e \frac{V_2}{V_1} \quad \text{or} \quad p_1V_1 \log_e \frac{V_2}{V_1}$$

$$\text{or} \quad = p_1V_1 \log_e \frac{p_1}{p_2} \quad \text{or} \quad p_1V_1 \log_e \frac{p_1}{p_2}$$

We are now ready to return to the evaluation of ${}_1Q_2$. Substitution of the known values of ΔE and ${}_1W_2$ for the change in the Non-Flow Energy Equation yields

$$J{}_1Q_2 = \underbrace{0}_{\Delta E} + \underbrace{p_1V_1 \log_e \frac{V_2}{V_1}}_{{}_1W_2}$$

$$\text{or} \quad {}_1Q_2 = \frac{p_1V_1}{J} \log_e \frac{V_2}{V_1}$$

The result shows that for a reversible non flow isothermal change of a gas the heat flow is equivalent to and has the same sign as the mechanical work performed.

Example

Five lb of nitrogen at 90° F expand at constant temperature from 168 lb per sq in. abs to 23 lb per sq in. gage. (a) How much work is done? (b) What are the sign and amount of heat flow accompanying the change?

Solution

$$\begin{aligned}
 \text{(a)} \quad p_1 &= 168 \times 144 \text{ lb per sq ft abs} \\
 V_1 &= ? \\
 p_2 &= 23 \times 144 \text{ lb per sq ft gage or } (23 + 14.7) \times 144 \text{ lb per sq ft abs} \\
 M &= 5 \text{ lb} \\
 B &= \frac{1544}{m}; m \text{ for } N_2 = 28 \\
 &= \frac{1544}{28} = 55.2 \text{ ft-lb per lb per } ^\circ R \\
 t &= 90^\circ F \\
 T_1 &= T_2 = 90^\circ + 460^\circ = 550^\circ R
 \end{aligned}$$

The initial volume may be obtained from the equation

$$\begin{aligned}
 p_1 V_1 &= MBT_1 \\
 168 \times 144 \times V_1 &= 5 \times 55.2 \times 550 \\
 V_1 &= 6.28 \text{ cu ft} \\
 &= \text{volume of 5 lb of } N_2 \text{ in state 1}
 \end{aligned}$$

Since the statement of the problem gives initial and final pressures rather than volumes, the expression for ${}_1W_2$ is

$$\begin{aligned}
 {}_1W_2 &= p_1 V_1 \log_e \frac{168}{37.7} \\
 {}_1W_2 &= 168 \times 144 \times 6.28 \times 2.3 \times \log_{10} \frac{168}{37.7} \\
 &= 168 \times 144 \times 6.28 \times 2.3 \times 0.649 \\
 &= 226,000 \text{ ft-lb}
 \end{aligned}$$

The solution might have been obtained even more easily by use of the equality between $p_1 V_1$ and MBT_1 . Thus

$$\begin{aligned}
 {}_1W_2 &= p_1 V_1 \log_e \frac{p_1}{p_2} \\
 \text{but } p_1 V_1 &= MBT_1 \\
 \text{so } {}_1W_2 &= MBT_1 \log_e \frac{p_1}{p_2} \\
 \text{and } {}_1W_2 &= 5 \times 55.2 \times 550 \times \log_e \frac{168}{37.7} \\
 &= 5 \times 55.2 \times 550 \times 2.3 \times 0.649 \\
 &= 226,000 \text{ ft-lb as before}
 \end{aligned}$$

(b) Since intrinsic energy change is zero for the isothermal process, the heat flow is equivalent to the work done. Also, because the process is an expansion, work is done by the medium on the surroundings and therefore is plus.

The sign of ${}_1Q_2$ must then also be plus which indicates that the work of expansion was done wholly at the expense of heat added while the change took place.

$$\begin{aligned} J{}_1Q_2 &= 0 + {}_1W_2 \\ &= 226\,000 \\ {}_1Q_2 &= \frac{226\,000}{778} = 290.5 \text{ Btu} \end{aligned}$$

The simple definition of entropy yields a direct means of computing the entropy change which accompanies any *reversible isothermal* change of state. For a non flow isothermal change of state of a perfect gas

$${}_1Q_2 = \frac{p_1 V_1}{J} \log_e \frac{V_2}{V_1}$$

Therefore, for such a change

$$\Delta S = \frac{{}_1Q_2}{T} = \frac{p_1 V_1 \log_e \frac{V_2}{V_1}}{JT}$$

Since $p_1 V_1 = MBT_1$

$$\frac{p_1 V_1}{T} = MB$$

whence

$$\Delta S = \frac{MB}{J} \log_e \frac{V_2}{V_1} = \frac{MB}{J} \log_e \frac{p_1}{p_2}$$

Non Flow Adiabatic Change of State of a Perfect Gas

Our first concern is to determine the particular form of the equation $pV^n = \text{const}$ which designates an adiabatic change of state of a perfect gas. We shall also consider that the change is *reversible*, thus eliminating the possibility of internal as well as external heat flow. For such a change ${}_1Q_2$ is zero by definition and so the Non Flow Energy Equation becomes

$$0 = \Delta E + {}_1W_2$$

or, for a differential change per pound of medium

$$\begin{aligned} 0 &= de + dw \\ &= Jc_v dT + p dv \end{aligned}$$

Now if we can express this equation in two variables instead of three, the result will integrate to an expression that will designate an adiabatic change. There is no difficulty in doing this for T is certainly a function of p and V . We also want the final result to apply specifically to the adiabatic change of a gas. Consequently, we use the *characteristic equation of a gas* to obtain the desired relationship for T in terms of p and V . Then, per pound of gas

$$\begin{aligned} pv &= BT \\ p dv + v dp &= B dT \\ \text{and} \quad dT &= \frac{p dv + v dp}{B} \end{aligned}$$

Substituting this relationship for dT in the preceding equation gives

$$Jc_v \left(\frac{pdv + vdp}{B} \right) + pdv = 0$$

$$\text{or } Jc_v(pd + vdp) + Bpdv = 0$$

$$\text{or } Jc_v vdp + (Jc_v + B)pdv = 0$$

On page 136 it was demonstrated that $B = J(c_p - c_v)$, and when this value of B is substituted in the differential equation, it becomes

$$Jc_v vdp + (Jc_v + Jc_p - Jc_v)pdv = 0$$

The equation may be further simplified by dividing through by Jc_v .

Then, remembering that $\frac{c_p}{c_v} = k$, we have

$$vdp + k pdv = 0$$

The variables of this equation may be readily separated, i.e.

$$\frac{dp}{p} + k \frac{dv}{v} = 0$$

and it may then be directly integrated. It is considered that k is constant, which it is for a perfect gas.

$$\int \frac{dp}{p} + \int k \frac{dv}{v} = 0$$

$$\log_e p + k \log_e v = C \text{ (a constant)}$$

Since the addition of logarithms implies the multiplication of factors

$$\log_e (pv^k) = C = \log_e (\text{const})$$

The antilogarithm of both sides of this equation yields an equation of the desired form, thus

$$pv^k = \text{const}$$

Hence, a non-flow adiabatic change of a perfect gas is characterized by the value $n = k = \frac{c_p}{c_v}$ for the exponent in $pV^n = \text{const}$.

In order to gain a clear conception of the relationship between pressure and volume during the adiabatic change of a perfect gas it is worth while to graph the equation as shown in Fig. 4-12. Suppose that air is compressed from an initial pressure of 10 lb per sq in. abs and an initial volume of 2 cu ft to a pressure of 30 lb per sq in. abs. Since the value of k for air is 1.4, the value of the constant in the adiabatic relationship is $10 \times 2^{1.4} = 27$. The volume in the second state may be determined from the equation, thus

$$30 \times V_2^{1.4} = 27$$

$$V_2 = 0.926 \text{ cu ft}$$

These figures show that during an adiabatic change of a perfect gas the volume changes in a less proportion than does the pressure. In the illustration, a threefold increase in pressure results in little more than a twofold decrease in volume. The same type of variation is exhibited by

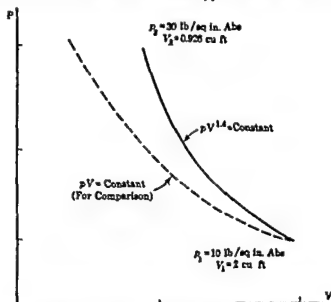


FIG. 4-12. Curve of Adiabatic Change for Gas and Comparison with Curve of Isothermal Change

any adiabatic change of a gas, because c_p is always greater than c_v and so k is always greater than 1. Consequently the curve representing such a change is steeper than the equilateral hyperbola representing the Boyle's Law equation, i.e., $pV = \text{const}$.

The differential equation from which $pV^k = \text{const}$ was obtained might just as well have been expressed in terms of T and p or T and V . Had this been done, the resulting equation would have been

$$TV^{k-1} = \text{const} \quad \text{in the first case, and}$$

$$Tp^{\frac{1-k}{k}} = \text{const} \quad \text{in the second}$$

Although $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$ is valid for a gaseous change of state of any character, there are times when the data are insufficient to make it of any use. In such cases, *when the change is a reversible adiabatic*, the above relations will be found decidedly useful. They may be combined with $pV^k = \text{const}$ to give the homogeneous expression

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{k-1} = \left(\frac{p_1}{p_2}\right)^{\frac{k-1}{k}}$$

The evaluation of the terms of the Non-Flow Energy Equation for an adiabatic change of a gas is a simple matter. The heat flow ${}_1Q_2$ is zero by the definition of the change. For reasons already given, the formula for intrinsic energy change is the same as for other gaseous changes of state, i.e.

$$\Delta E = \frac{p_2 V_2 - p_1 V_1}{k - 1}$$

Consequently, the formula for ${}_1W_2$ may be obtained thus

$$0 = \frac{p_2 V_2 - p_1 V_1}{k - 1} + {}_1W_2$$

$${}_1W_2 = - \frac{p_2 V_2 - p_1 V_1}{k - 1} = \frac{p_2 V_2 - p_1 V_1}{1 - k}$$

Expressed otherwise, this result means that *any work done during a non-flow adiabatic change is equivalent to the negative of the intrinsic energy change of the process*. The expression for ${}_1W_2$ might also have been obtained by integrating the work function ${}_1W_2 = \int p dV$ over the path $pV^k = \text{const.}$ We have already carried out this integration (pages 45-46) for the typical path $pV^n = \text{const.}$ when n has a value other than 1. Since k is always greater than 1, the result previously obtained is entirely valid here if k is substituted for n . The formula obtained on page 46 is

$${}_1W_2 = \frac{p_2 V_2 - p_1 V_1}{1 - n}$$

With k substituted for n , we have

$${}_1W_2 = \frac{p_2 V_2 - p_1 V_1}{1 - k} \text{ as obtained above}$$

Example

Four cu ft of air at 80 lb per sq in. gage pressure are expanded without loss or gain of heat to a pressure of 15 lb per sq in. abs. How much work is done?

Solution

$$p_1 = 80 + 14.7 = 94.7 \text{ lb per sq in. abs or } 94.7 \times 144 \text{ lb per sq ft abs}$$

$$V_1 = 4 \text{ cu ft}$$

$$p_2 = 15 \text{ lb per sq in. abs or } 15 \times 144 \text{ lb per sq ft abs}$$

$$V_2 = ?$$

$$k_{\text{air}} = \frac{c_p}{c_v} = 1.4$$

The second volume, V_2 , may be readily determined from the equation $pV^k = \text{const.}$ Thus

$$p_1 V_1^k = p_2 V_2^k \quad \text{or} \quad \frac{p_1}{p_2} = \left(\frac{V_2}{V_1} \right)^k$$

Substituting, we have

$$\frac{94.7 \times 144}{15 \times 144} = \left(\frac{V_2}{4}\right)^{1.4}$$

or
$$\left(\frac{94.7}{15}\right)^{\frac{1}{1.4}} = \frac{V_2}{4}$$

Hence
$$3.7 = \frac{V_2}{4}$$

$$V_2 = 14.8 \text{ cu ft}$$

Substitution of this value, together with the given data, in the adiabatic work equation gives

$$\begin{aligned} {}_1W_2 &= \frac{15 \times 144 \times 14.8 - 94.7 \times 144 \times 4}{1 - 1.4} \\ &= \frac{32,000 - 54,500}{-0.4} \\ &= \frac{-22,500}{-0.4} = +56,250 \text{ ft lb} \end{aligned}$$

When we come to apply the Second Law of Thermodynamics to the change under discussion we are considerably aided by the previous discussion of reversible adiabatic processes (page 72). It was there established that such a process is characterized by constancy of entropy, i.e.

$$\Delta S = 0$$

There is no heat flow, internally or externally, in a reversible adiabatic change. Consequently, when a gas is compressed by such a process, there is *no change in the availability* of the work done on the system. Upon reversible expansion, *all* of the energy stored as intrinsic energy is available for the performance of external work. This is true whether or not the medium is a gas. The conclusion is therefore general rather than specific in nature. As such, it must be carefully distinguished from the considerable number of relationships which have been set forth in this chapter and which pertain *only to gases*.

Non-Flow Polytropic Change of State of a Perfect Gas

Since the polytropic change of state is the one most frequently encountered in actual thermodynamic cycles, the study of the application of the First and Second Laws to it is of considerable practical significance. By definition (pages 38-39) a non-flow polytropic change is *not* characterized by the constancy of any coordinate (see Fig. 4-13). It is therefore fruitless to make any attempt to *derive* the value of n in $pV^n = \text{const}$ which designates it. Actual experimental measurement of p and V at two different state points of the change is the only basis upon which n

for this change can be determined. The computation of n from these data is then made by the method given on page 39; the result will be different for different conditions of p and V . It is assumed that the value of n determined in this way is *constant throughout the change*, an assumption

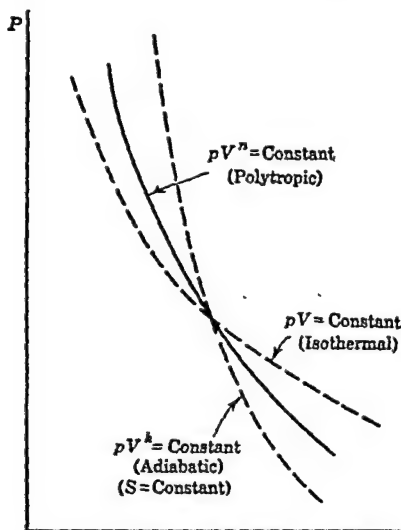


FIG. 4-13. Curve of Polytropic Change for Gas and Comparison with Curves of Adiabatic and Isothermal Changes.

which is usually in accord with the facts. In conclusion, then, a *non-flow polytropic change may be characterized by any constant value of n in $pV^n = \text{const.}$*

The combination of $pV^n = \text{const.}$ with the characteristic equation of a perfect gas, $pV = MBT$, makes it possible to obtain the following equations which describe the polytropic change of a gas in terms of T and V and T and p respectively:

$$TV^{n-1} = \text{const}$$

and

$$Tp^{\frac{1-n}{n}} = \text{const}$$

These equations are the same as the corresponding ones for the adiabatic change, except that n is everywhere substituted for k . As with the adiabatic equations, the present ones may be combined into the homogeneous relationship

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{n-1} = \left(\frac{p_1}{p_2}\right)^{\frac{n-1}{n}}$$

The usefulness of these relationships may be illustrated as follows. Suppose that a gas changes state according to the equation $pV^{1.25} = \text{const.}$

The initial temperature T_1 and the pressure p_1 are known, as is also the final pressure p_2 . The only way of determining the final temperature T_2 with these data is by means of the relation

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{n-1}{n}}$$

which, since $n = 1.25$, becomes

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{1.25-1}{1.25}}$$

The terms of the Non-Flow Energy Equation for a non-flow polytropic change of a perfect gas are best evaluated by dealing first with ΔE and ${}_1W_2$. This is so because the evaluation of ${}_1Q_2$ in terms of temperature requires knowledge of c_n , the specific heat for the process, which is as yet unknown. We shall see, however, that a formula for c_n may be determined by consideration of all the energy quantities involved in the change.

As for any change of a perfect gas, ΔE is given by

$$\Delta E = E_2 - E_1 = \frac{p_2 V_2 - p_1 V_1}{k - 1}$$

We have already evaluated ${}_1W_2 = \int p dV$ for a change designated by $pV^n = \text{const}$, with n having a constant value other than 1 (page 45). This is *exactly* the condition that describes the change now being considered. Therefore ${}_1W_2$ for the non flow polytropic change of a perfect gas is given by

$${}_1W_2 = \frac{p_2 V_2 - p_1 V_1}{1 - n}$$

Great care should be taken to distinguish clearly between this formula and the one for ΔE . In the denominator of the expression for ΔE is the factor k , which equals $\frac{c_p}{c_v}$ and is a *single value* constant for a perfect gas.

Its value has *nothing* to do with the type of change under consideration. The factor n in the denominator of the formula for ${}_1W_2$ depends *wholly* on the nature of the change, and for a polytropic change has a value determined by experiment for that particular change alone.

When the formulas obtained for ΔE and ${}_1W_2$ are substituted in the Non-Flow Energy Equation, there results

$${}_1Q_2 = \frac{p_2 V_2 - p_1 V_1}{k - 1} + \frac{p_2 V_2 - p_1 V_1}{1 - n}$$

The equation may be simplified by factoring out the common quantity $(p_2V_2 - p_1V_1)$. Then

$$J_1Q_2 = \frac{k-n}{(k-1)(1-n)} (p_2V_2 - p_1V_1)$$

It is now an easy matter to establish, in terms of k and n , the ratio between ${}_1W_2$ and ΔE , ${}_1W_2$ and J_1Q_2 , or J_1Q_2 and ΔE for a polytropic process, all of which are frequently used relationships. Thus

$$\frac{{}_1W_2}{\Delta E} = \frac{\frac{p_2V_2 - p_1V_1}{1-n}}{\frac{p_2V_2 - p_1V_1}{k-1}} = \frac{k-1}{1-n}$$

$$\frac{{}_1W_2}{J_1Q_2} = \frac{\frac{p_2V_2 - p_1V_1}{1-n}}{\frac{(k-n)(p_2V_2 - p_1V_1)}{(k-1)(1-n)}} = \frac{k-1}{k-n}$$

and

$$\frac{J_1Q_2}{\Delta E} = \frac{\frac{(k-n)(p_2V_2 - p_1V_1)}{(k-1)(1-n)}}{\frac{p_2V_2 - p_1V_1}{k-1}} = \frac{k-n}{1-n}$$

Moreover, the equation for J_1Q_2 in terms of p , V , k , and n may readily be transformed into one in terms of mass, temperature, and specific heat by the application of the characteristic equation $pV = MBT$. Thus

$$p_1V_1 = MBT_1; p_2V_2 = MBT_2$$

so

$$J_1Q_2 = \frac{k-n}{(k-1)(1-n)} [MB(T_2 - T_1)]$$

or

$${}_1Q_2 = M \frac{\frac{B}{J} (k-n)}{(k-1)(1-n)} (T_2 - T_1)$$

Since in general ${}_1Q_2 = Mc(T_2 - T_1)$, in which c is the *specific heat for the process*, it follows that for a non-flow polytropic change of a gas, the specific heat for the process c_n is given by

$$c_n = \frac{\frac{B}{J} (k-n)}{(k-1)(1-n)}$$

This may be simplified by use of the relations

$$\frac{B}{J} = (c_p - c_v) \text{ and } k = \frac{c_p}{c_v}$$

Then
$$\frac{\frac{1}{J}B}{k-1} = \frac{c_p - c_v}{\frac{c_p}{c_v} - 1} = \frac{c_p - c_v}{(c_p - c_v)/c_v} = c_v$$

Consequently
$$c_n = c_v \left(\frac{k-n}{1-n} \right)$$

Therefore the value of the specific heat for a gaseous polytropic process may be computed from knowledge of c_v , the ratio $\frac{c_p}{c_v}$, and the value of the exponent n . With the value of c_n obtained in this manner, ${}_1Q_2$ may be directly computed by substitution in

$${}_1Q_2 = Mc_n(T_2 - T_1)$$

For values of n between 1 and k , c_n is evidently negative. This result may appear startling at first, but a little study shows that it is perfectly reasonable. Take, for example, polytropic expansion, with $1 < n < k$. The work done by the medium represents a greater amount of energy than does the heat added during the process by the ratio

$$\frac{{}_1W_2}{{}_1Q_2} = \frac{k-1}{k-n}$$

The difference must be supplied at the expense of a decrease in the store of intrinsic energy. A decrease in intrinsic energy means a decrease in temperature. Consequently, even though heat is supplied during the process, the temperature falls, and therefore the specific heat for the process is negative.

The use of the various formulas for the non flow polytropic change of a perfect gas is illustrated in the following example.

Example

A polytropic line on a pV diagram represents the expansion of 2 lb of oxygen. In the initial state the pressure is 100 lb per sq in abs, and the volume is 4 cu ft. In the final state the pressure is 5 lb per sq in gage and the volume is 15 cu ft. (a) How much work is done? (b) What are the amount and sign of the change in intrinsic energy? (c) Is heat added or withdrawn and in what amount? (d) What is the specific heat c_n for the process?

Solution

$$p_1 = 100 \text{ lb per sq in. abs, or } 100 \times 144 \text{ lb per sq ft abs}$$

$$V_1 = 4 \text{ cu ft}$$

$$p_2 = (5 + 14.7) \text{ lb per sq in. abs} = 19.7 \times 144 \text{ lb per sq ft abs}$$

$$V_2 = 15 \text{ cu ft}$$

$$k_{O_2} = 1.4$$

$$c_v = 0.16$$

$$B = \frac{15.44}{32} = 48.25$$

$$n = \frac{\log p_1 - \log p_2}{\log V_2 - \log V_1} = \frac{\log \frac{p_1}{p_2}}{\log \frac{V_2}{V_1}} = \frac{\log_{10} \frac{100 \times 144}{19.7 \times 144}}{\log_{10} \frac{15}{4}}$$

$$= \frac{0.7055}{0.574} = 1.23$$

$$(a) {}_1W_2 \text{ (polytropic)} = \frac{p_2 V_2 - p_1 V_1}{1 - n}$$

$$= \frac{19.7 \times 144 \times 15 - 100 \times 144 \times 4}{1 - 1.23}$$

$$= \frac{144(19.7 \times 15 - 100 \times 4)}{1 - 1.23}$$

$$= \frac{-15,040}{-0.23}$$

$$= 65,500 \text{ ft-lb}$$

$$(b) \Delta E = \frac{p_2 V_2 - p_1 V_1}{k - 1} = \frac{19.7 \times 144 \times 15 - 100 \times 144 \times 4}{1.4 - 1}$$

$$= \frac{-15,040}{+0.4} = -37,600 \text{ ft-lb}$$

Hence ΔE decreases by 37,600 ft-lb.

(c) The amount and nature of the heat flow may be obtained quickly from the algebraic sum of ΔE and ${}_1W_2$, thus

$$J_1 Q_2 = -37,600 + 65,500 = 27,900 \text{ ft-lb}$$

$$\text{or } {}_1Q_2 = \frac{27,900}{778} = +35.9 \text{ Btu}$$

This result means that 35.9 Btu must be added during the expansion.

$$(d) c_n = c_v \frac{k - n}{1 - n} = 0.16 \frac{1.4 - 1.23}{1 - 1.23}$$

$$= \frac{0.16 \times 0.17}{-0.23} = \frac{0.0272}{-0.23} = -0.118$$

It is instructive to use this value of c_n to compute the heat flow and thereby check the result obtained in (c). The initial and final temperature may be found from $pV = MBT$.

$$p_1 V_1 = MBT_1 \qquad p_2 V_2 = MBT_2$$

$$100 \times 144 \times 4 = 2 \times 48.25 \times T_1; \quad 19.7 \times 144 \times 15 = 2 \times 48.25 \times T_2$$

$$T_1 = 597^\circ \text{ R} \qquad T_2 = 442^\circ \text{ R}$$

Then, by substitution in ${}_1Q_2 = Mc_s(T_2 - T_1)$

$$\begin{aligned} {}_1Q_2 &= 2 \times (-0.118)(442 - 597) \\ &= +36.5 \text{ Btu} \end{aligned}$$

The agreement of this result with the preceding one is within the error in the values of c_s and k which were used

As for any reversible change, the application of the Second Law to a non flow reversible polytropic change involves only the determination of an expression which will permit computation of the entropy change of the medium for the process. From this information and knowledge of the lowest available constant temperature to which a cycle involving the process could reject heat, it is possible to determine at once the availability of the heat added. Since the temperature changes during a polytropic change, we must start with the differential expression for entropy change, i.e.

$$dS = \frac{\delta Q}{T}$$

For a polytropic process, $\delta Q = Mc_s dT$

Then
$$dS = \frac{Mc_s dT}{T}$$

If c_s is constant

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{Mc_s dT}{T} = Mc_s \log_e \frac{T_2}{T_1}$$

When $1 < n < k$, T_2 is less than T_1 and so $\log_e \frac{T_2}{T_1}$ is minus. But under these conditions c_s is also minus and so ΔS is plus as it must be whenever heat is added to a medium.

The student will find it profitable to gather together the various formulas for non flow gaseous change of state and record them in the indicated spaces in Table 4-3

PROBLEMS

- 1 What is a characteristic equation, and how is it determined?
- 2 The weight of air under normal pressure and temperature is 0.08071 lb per cu ft. Compute the gas constant for air.
- 3 The compressibility factor of N_2 at 1 atm and $0^\circ C$ is 0.999. At a pressure of 50 atm and $-50^\circ C$ it is 0.94. It is desired to have 10 liters of the gas in the latter condition. Compute (a) the weight of nitrogen present, (b) the volume this quantity of N_2 occupies at standard conditions in cgs units $R = 82.06$ cc atm per mol per $^\circ K$.
- 4 If B for air is 53.35, calculate the molar weight of air.
- 5 Ten lb of air are heated at constant pressure of 200 lb per sq in. from 50° to $60^\circ F$. (a) How much heat energy has been supplied if $c_p = 0.242$? (b) What would be the effect on the computation of (a) if c_p is taken as $f(T)$? (c) How much of the heat energy supplied is stored in the air as intrinsic energy?
- 6 The volume of a quantity of air is 10 cu ft at a temperature of $60^\circ F$ when the pressure is 15 lb per sq in. abs. (a) What is the pressure of this air when the volume becomes 60 cu ft and the temperature $60^\circ F$? (b) What is the weight of the air?
- 7 At what temperature will 50 lb of air occupy 60 cu ft when at absolute pressure of 20 lb per sq in.? $B = 53.35$ for air.
- 8 One lb of hydrogen is cooled at constant pressure from a volume of 1 cu ft and a temperature of $300^\circ F$ to a temperature of $60^\circ F$. What is the resulting volume?
- 9 Three lb of air are compressed from a volume of 2 to 1 cu ft at a constant temperature of $60^\circ F$. How many Btu of heat must be rejected from the air?
- 10 It is desired to have 10 lb of H_2 at 250 lb per sq in. abs and $60^\circ F$. The compressor takes H_2 at $60^\circ F$ and at atmospheric pressure of 15 lb per sq in. abs and compresses along the curve $pV^{1.2} = \text{const}$. What must be the pressure at delivery from the compressor in order that the compressed H_2 shall cool to the desired conditions at a constant volume in the receiver?
- 11 If the initial condition of an ideal gas is such that the volume is 6 cu ft and the gas is compressed to 1.4 cu ft at a constant pressure of 50 lb per sq in. gage, compute the intrinsic energy change and the heat which must be abstracted by the cooling agent in order to keep the pressure constant. $k = 1.4$.
- 12 The Universal Gas Constant R for all gases is given in cgs units as 2 cal per g mol per $^\circ C$. By conversion of this value and by means of the relation between B and R , find the value of B for nitrogen (mol wt = 28) in ft lb per lb per $^\circ F$.
- 13 Calculate the pressure necessary to compress 100 liters of N_2 at a pressure of 760 mm of Hg and a temperature of $23^\circ C$ to a volume of 1.0 liter at $-50^\circ C$. (a) Make the calculation with the Perfect Gas Law. (b) Make the calculation with compressibility factors.

$$C_{p, \text{state 1}} = 1.00$$

$$C_{p, \text{state 2}} = 0.92$$

14. Four lb of air ($k = 1.4$, $B = 53.3$) at 20°C are compressed from a pressure of 15 lb per sq in. abs to 100 lb per sq in. abs. Compute the work done on the air when the change is (a) isothermal; (b) adiabatic.
- (15) a. Given the equation ${}_1W_2 = \int_1^2 p dV$, evaluate the work for the following changes of state for an ideal gas, considering the general equation for change of state of an ideal gas to be $pV^n = \text{const}$: (1) Pressure constant; (2) volume constant; (3) pV constant (isothermal); (4) pV^k constant (adiabatic); (5) pV^n constant (polytropic).
- (b) Derive the expression for intrinsic energy change for the above changes of state.
- (16) Define isothermal, adiabatic, isopiestic, isometric, and polytropic changes of state. Sketch the curve for each of these changes for a perfect gas on pV and TS planes, and give the equations of the path for each change.
17. Why is the integrated form of dE the same for all types of change of a perfect gas except the isothermal? Why does its value differ for the isothermal change?
18. Describe an experiment which shows that the intrinsic energy change of a perfect gas is a function of the temperature change only.
19. One cu ft of air at a pressure of 150 lb per sq in. abs expands isothermally to a pressure of 50 lb per sq in. abs. Calculate the work done and the heat added during the expansion.
20. Discuss the meaning and use of compressibility factors.
21. Four lb of nitrogen, which may be considered as an ideal gas, are at a temperature of 60°F and a pressure of 80 lb per sq in. abs. Compare the work done by an expansion to 15 lb per sq in. abs when isothermal; when adiabatic. How much heat must be supplied in order that the change shall take place according to the equation $pV^{1.2} = \text{const}$?
22. What is the increase in entropy of 4 lb of air when heated from 50°F to 450°F ? (a) At constant pressure? (b) At constant volume?
23. Fifteen lb of oxygen ($B = 48.25$) are in a container at a pressure of 250 lb per sq in. abs and at atmospheric temperature of 60°F . The process in which the O_2 is to be used requires an initial pressure of 350 lb per sq in. abs which is attained by heating the gas at constant volume. (a) What is the volume of the container? (b) How much heat is added and what is the resultant change in intrinsic energy? (c) What is the entropy change? (d) The compressed O_2 expands to atmospheric pressure (14.0 lb per sq in.), at which time its temperature is -80°F . How much of the heat previously added is available for doing external work during the expansion?
24. One lb of air expands at a constant *gage* pressure of 150 lb per sq in. at sea level, from 1.2 to 3.8 cu ft. Compute the change in entropy.
25. Compute the apparent molecular weight and the gas constant B for a gas of the following composition by volume:

$$\begin{aligned} \text{H}_2 &= 0.06 \\ \text{CO} &= 0.28 \\ \text{CO}_2 &= 0.10 \\ \text{N}_2 &= 0.56 \end{aligned}$$

- 26 Five lb of air are compressed adiabatically from 15 lb per sq in abs at 70° F to 450 lb per sq in abs. Find the final temperature (a) if the specific heat of air is assumed to be constant, (b) by using the variable specific heat expression

$$\left(a' + \frac{B}{J}\right) \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2) = \frac{B}{J} \ln \frac{p_2}{p_1}$$

- 27 What is the meaning of c_p and c_v (a) in terms of partial derivatives? (b) in physical significance? (c) What is the relation between these quantities for the three states or phases of matter? (d) Which is larger, and why?
- 28 One lb of air expands at sea level at a constant gage pressure of 150 lb per sq in from 1.2 to 3.8 cu ft. For air $c_p = 0.24$. (a) Compute the change in entropy. What practical use may be made of this result? (b) Is heat added or abstracted, and how much? (c) What is the change in intrinsic energy in sign and in amount? (d) What is the change in temperature? (e) How much work is done and what is its sign?
- 29 Why is less work required in compressing air to a given pressure isothermally than is required when the process is carried out adiabatically?
- 30 What fraction of heat supplied a system goes to external work done by the system in a change which is (a) isothermal, (b) isopiestic, (c) isometric, (d) polytropic? Express as a ratio involving k or n , or both.

Thermodynamic Properties of Vapors; Vapor Change of State

Nature of a Vapor

The preceding detailed application of the First and Second Laws to a gaseous change of state was *strictly limited* to substances that behaved reasonably in accord with the Perfect Gas Law. This law is *grossly inaccurate* for describing the behavior of a medium in the gaseous phase when conditions for liquefaction are approached. In order to emphasize this difference in behavior, a medium in the latter condition is no longer called a gas but is designated by the name *vapor*. The distinction between a gas and a vapor is not sharply drawn; it is simply a matter of the relative state of a medium with respect to its critical state. As an illustration, air at room temperature is a gas, but as liquid air evaporates into the gaseous phase it forms a vapor.

Because of the failure of the Perfect Gas Law to describe the behavior of a vapor, the formulas for ${}_1Q_2$, ΔE , and ${}_1W_2$ obtained in Chapter 4 are worthless for a vapor change of state. Other means, which take into account the characteristic properties of vapors, must be determined for evaluating these quantities. It is the object of this chapter to present in detail how this may be done.

Characteristic Equations of Vapors

At the outset we must bear in mind that each medium has its own characteristic equation. When dealing with gases to which the Perfect Gas Law may be reasonably well applied, the constant B is the factor that varies with the nature of the gas. In the more complicated van der Waal Equation, the constants a and b have values which are decidedly different for different gases. The influences affecting the behavior of a medium become increasingly complex as the conditions for liquefaction are approached, and consequently it is not surprising that the characteristic equations for vapors should involve a number of constants whose values vary widely with the nature of the medium. More than this, and also because of the complexity of the forces whose action it describes, the characteristic equation of a vapor is algebraically

complicated. For these reasons, there is no simple equation which we may use to characterize vapors as a class in the way that we use the Perfect Gas Law in connection with gases. We must deal with each vapor separately, and since steam is the vapor with the widest industrial use, we shall limit the present discussion to it. Meanwhile, we must keep in mind the fact that the application of the thermodynamic laws to water vapor is to be considered not only for its own sake, but also, and more generally, as illustrative of the method of application to other vapors, such as ammonia and sulphur dioxide.

This thought may be generalized even further. So far as the nature of thermodynamics is concerned, there is *no requirement* that the medium shall be in the gaseous phase. Its laws can be and are profitably applied to liquid and solid media and the method of application is, in a general way, the same as it is for gaseous and vapor media. However, it is a fact that, because of their great mobility, gases and vapors have a much broader industrial use than liquids and solids. It is proper, therefore, to choose them to exemplify the procedure by which the general laws may be applied to any medium, whatever its nature or state of aggregation. We proceed, then, to a consideration of the properties of water vapor.

Properties of Water Vapor

It is common experience that the temperature of boiling water is fixed by the pressure. On top of a mountain where the atmospheric pressure is low the boiling point is also low, and so, for example, a longer time is required to cook eggs to the desired degree of consistency than at sea level. Thermodynamically this is expressed by saying that for the process of evaporation, pressure is a function of temperature only, a relationship which is true for the evaporation of any liquid. The exact nature of this relationship for the temperature range 50°C to 374.11°C is given by empirical equations such as the following one, used by Keenan and Keyes* and developed by measurements made by Smith, Keyes, and Gerry†

$$\log_{10} \frac{p_i}{p} = \frac{x}{T} \left(\frac{a + bx + cx^2 + ex^3}{1 + dx} \right)$$

in which p = the vapor pressure in international atmospheres‡

* J. H. Keenan and F. G. Keyes, *Thermodynamic Properties of Steam*, Wiley, p. 14.

† L. B. Smith, F. G. Keyes and H. T. Gerry, *Proc. Am. Acad. Arts and Sci.*, 69, 137 (1934).

‡ The international atmosphere is defined as the pressure produced by a column of mer-
cury 760 mm high at zero centigrade where the gravitational acceleration is 980.665 cm per
sec².

p_c = the critical pressure = 218.167 internat atm

T = the temperature in degrees Kelvin

$x = (T_c - T)$ where T_c is the critical temperature in degrees Kelvin

$a = 3.3463130$

$b = 4.14113 \times 10^{-2}$

$c = 7.515484 \times 10^{-9}$

$d = 1.3794481 \times 10^{-2}$

$e = 6.56444 \times 10^{-11}$

Similar empirical formulas for other temperature ranges have been obtained. The one given, however, suffices to show how laborious a task it would be to make the necessary computation every time one wanted to determine the evaporation temperature from knowledge of the pressure. Thanks to extensive researches on the properties of steam, culminating in the recent American steam research program, this is not necessary. Extensive tables have been prepared with the aid of computing machines which list the pressure and corresponding temperature of evaporation of steam for absolute pressures from 0.25 in. of Hg to 3206.2 lb per sq in. The student will find these values in the first two columns of the *Abridged Edition of Steam Tables* in the appendix of this book.

Clapeyron Equation

Sometimes it is of importance to determine the rate of change in the boiling point with pressure. For steam, this may be done by reference to the steam tables, but for other vapors for which tables are not available, the Clapeyron Equation provides a useful, although *approximate*, relationship. Its derivation is accomplished by setting up a theoretical reversible cycle for the evaporation process. The changes of this cycle are illustrated in Fig. 5-1. Consider that a unit mass of liquid just at the boiling point T is designated by state point 1 in the diagram. Let this liquid be completely evaporated reversibly as shown by the path 1-2. Both temperature T and pressure p remain constant during the process. Then let the pressure be decreased at a constant volume by an infinitesimal amount Δp (state point 3). Since the temperature of evaporation varies with pressure, the vapor is now at a temperature $T - \Delta T$ infinitesimally below the boiling point. Hence it starts to condense. Let the process of condensation continue reversibly at the lower constant pressure $p - \Delta p$ and temperature $T - \Delta T$ until state point 4 is reached. An infinitesimal increase in the pressure Δp with the volume constant

then restores the medium to its initial state. Since each of these processes has been accomplished reversibly, the cycle has the same efficiency as

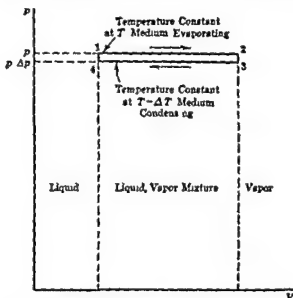


FIG. 5-1 Diagram of a Theoretical Reversible Cycle for the Evaporation Process

a Carnot cycle operating between temperatures T and $T - \Delta T$. The efficiency is therefore

$$\eta = \frac{T - (T - \Delta T)}{T} = \frac{\Delta T}{T}$$

The latent heat of the fluid per unit of weight, designated by L , is the heat added to the cycle during evaporation (isothermal expansion). The product of L multiplied by Carnot efficiency then gives the net work of the cycle

$$L \frac{\Delta T}{T} = \frac{W_{\text{cycle}}}{J}$$

The equation now is in terms of temperature, heat and work. We want the final result to involve both temperature and pressure. We may introduce pressure into the equation by evaluating the work of the cycle from the pV diagram. Thus, the work done by the medium during evaporation is equal to

$$p(v_2 - v_1)$$

The work done on the medium during condensation is equal to

$$(p - \Delta p)(v_3 - v_4)$$

and hence the work of the cycle is

$$W_{\text{cycle}} = p(v_2 - v_1) - (p - \Delta p)(v_3 - v_4)$$

But

$$(v_3 - v_4) = (v_2 - v_1)$$

so the net work of the cycle is equal to

$$W_{\text{cycle}} = (v_2 - v_1)(p - p + \Delta p) = \Delta p(v_2 - v_1)$$

If this value for the work done is substituted for W in the preceding equation there results

$$L \frac{\Delta T}{T} = \frac{W}{J} = \frac{\Delta p}{J} (v_2 - v_1)$$

The whole purpose of setting up the cycle was to ascertain the relationship between pressure and temperature of evaporation. Hence the equation may be rearranged to give the relation known as the Clapeyron Equation, thus

$$\frac{\Delta p}{\Delta T} = \frac{JL}{T(v_2 - v_1)}$$

Although the object of deriving the Clapeyron Equation was to determine the pressure-temperature relationship for evaporation, this equation proves to be useful also for the computation of latent heat. The ratio $\frac{\Delta p}{\Delta T}$, the absolute temperature T , and the specific volumes v_2 and v_1 are all directly measurable quantities. When they are known, direct substitution in the Clapeyron Equation gives the value of the latent heat per unit mass at the temperature T . The equation may also be used for *any* change of phase, and so it applies to problems involving the process of fusion as well as to those concerned with the process of evaporation. The following example illustrates its use.

Example

The vapor pressure of liquid ammonia is 7.6 atm at 17° C and increases at the rate of 0.25 atm per degree centigrade. The specific volumes of vapor and liquid are respectively 165 cc per g and 2 cc per g. Calculate the heat of vaporization per gram of ammonia.

Solution

Since the data give pressures in units of atmospheres and the change in volume in cc, the unit of work is the cc atmosphere. Therefore the conversion factor J is the number of cc atmospheres per gram-calorie, i.e., 41.3. Direct substitution in the equation gives

$$0.25 \quad \underline{\quad 41.3 \times L \quad}$$

Clausius Clapeyron Equation

The ratio $\frac{\Delta p}{\Delta T}$ determined by the Clapeyron Equation has different values at different temperatures. It is *not possible* to determine it at one temperature T_1 , multiply by the interval between T_1 and some other temperature T_2 , and thereby obtain the change of evaporation pressure corresponding to the temperature interval. Clausius showed that if the Clapeyron Equation were treated as a differential equation it might be integrated, with the aid of certain bold assumptions, to yield an equation involving evaporation pressures and temperatures in two corresponding states rather than $\frac{\Delta p}{\Delta T}$. First, then, let us rewrite the Clapeyron Equation as

$$\frac{dp}{dT} = \frac{JL}{T(v_2 - v_1)}^*$$

Second, although the equation applies to a medium undergoing evaporation, let us make the seemingly unwarranted assumption that the Perfect Gas Law applies. Third, let us assume that the specific volume of the liquid v_1 is negligible. Then by these assumptions

$(v_2 - v_1) = \text{volume } v \text{ of a unit mass of a perfect gas at temperature } T$
By the Perfect Gas Law

$$v = \frac{BT}{p}$$

Substituting this value gives

$$\frac{dp}{dT} = \frac{JL}{T \times \frac{BT}{p}}$$

By separating the variables p and T , we obtain

$$\frac{dp}{p} = \frac{JL}{B} \frac{dT}{T^2}$$

This equation is readily integrable between the limits p_1 , T_1 , and p_2 , T_2 thus

$$\begin{aligned} \log_e \frac{p_2}{p_1} &= \frac{JL}{B} \int_{T_1}^{T_2} \frac{dT}{T^2} = \frac{JL}{B} \left(-\frac{1}{T} \right)_{T_1}^{T_2} = \frac{JL}{B} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ &= \frac{JL}{B} \left(\frac{T_2 - T_1}{T_1 T_2} \right) = \frac{JmL}{mB} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \text{ in work units} \\ &= \frac{mL}{2} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \text{ in heat units} \end{aligned}$$

where m is the molecular weight

* It is possible to make a rigorous derivation of the equation in this form.

Although two of the assumptions upon which this integration is made seem to contradict flatly all that has been said regarding the relative behavior of vapors and gases, the resulting equation is sufficiently accurate to be useful in dealing with media for which vapor tables have not been prepared. In particular, it is used to determine the vapor pressure of a substance at a lower temperature than the boiling point from knowledge of boiling-point data.

Example

The heat of vaporization of water at 760 mm pressure and 100° C is 538 cal per g. Calculate the vapor pressure of water at 80° C.

Solution

In order to simplify calculations, invert the equation given on page 166; i.e., write it in the following form and express it in heat units.

$$\log_e \frac{p_1}{p_2} = \frac{JL}{B} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

$$\begin{array}{ll} p_1 = 760 \text{ mm} & T_1 = 100 + 273 = 373^\circ \text{ K} \\ p_2 = ? & T_2 = 80 + 273 = 353^\circ \text{ K} \end{array}$$

$$\frac{1}{J} B = \frac{\frac{1}{J} R}{m} = \frac{2 \text{ cal}}{18} = 0.111 \text{ cal per g}$$

$$\log_e \frac{760}{p_2} = \frac{538}{0.111} \left[\frac{373 - 353}{(373)(353)} \right]$$

$$= \frac{538 \times 20}{(0.111)(373)(353)} = 0.734$$

$$\frac{760}{p_2} = 2.082$$

$$p_2 = 365 \text{ mm of Hg}$$

The Steam Tables

All of the equations for the various properties of steam are fully as complicated as the one for the pressure-temperature relationship. Consequently their values are listed in tables in order to avoid endless and tedious repetition of computing them. Of course, only point functions are susceptible of tabulation and space limitations are such that it is not profitable to list all of them. The tabulation of pressure and corresponding temperature of evaporation has already been mentioned. There is evident need of listing values of the third elementary coordinate, volume, for each state. Since enthalpy h measures the path function ${}_1Q_2$ for the commonly encountered constant-pressure change (see page 85) it is desirable to have its values. Also, knowledge of the enthalpy, pressure, and specific volume in a certain state makes it rather easy to compute the intrinsic energy from $h = e + \frac{pv}{J}$. Hence, values

for e are not always given. Finally, the availability of the heat added in achieving a certain state can be determined only through knowledge of the entropy change produced. Thus, values of entropy have a proper, and indeed indispensable, place in the tables.

The abridged edition of Keenan's steam tables shows the following headings in Table I for saturated steam

Temp Deg F t	Abs Press Lb per Sq In p	Specific Volume			Enthalpy		
		Sat Liquid	Evap	Sat Vapor	Sat Liquid	Evap	Sat Vapor
		v_f	v_{fg}	v_g	h_f	h_{fg}	h_g
		Entropy					
		Sat Liquid	Evap	Sat Vapor			
		s_f	s_{fg}	s_g			

These tables are referred to a datum temperature of 32° F. Thus, the listed values of enthalpy and entropy represent $h_2 - h_1$ and $s_2 - s_1$ where h_1 and s_1 are the respective values when the medium is at 32° F. The values given in the tables also refer to the properties of one pound of steam. The volume, enthalpy, or entropy of M pounds may be found by multiplying the listed values by M . The term saturated liquid — subscript f — denotes the properties of water just at the boiling point. The term evaporation — subscript fg — refers to the change in each property that takes place as the medium goes from the condition of saturated liquid to that of saturated vapor, i.e., to the point at which the last molecule of water is evaporated. The term saturated vapor — subscript g — designates the state in which the medium is completely evaporated but is still at the temperature of evaporation.

Frequently it is necessary to deal with a mixture of steam and water, a condition that results when the evaporation is not complete. In such a case the medium is said to be a *wet vapor*. The degree of completion of the evaporation process in a wet vapor is quantitatively established by its *quality* x . By definition, x is taken to be the ratio between the weight of steam formed and the total weight of steam and water present in the mixture. Thus, a mixture made up of $\frac{1}{10}$ lb of steam and $\frac{1}{10}$ lb of water would have a quality of

$$x = \frac{\frac{1}{10}}{\frac{1}{10} + \frac{1}{10}} = \frac{1}{2} = 0.50$$

Table 2 of the steam tables lists the same quantities as Table 1, except values of internal or "intrinsic" energy, u_f and u_g , are added for the saturated liquid and saturated vapor state. u_{fg} has been omitted here

because of space requirements, but can easily be obtained by subtracting v_f from v_g (see the following example). The usefulness of Table 2 lies in the fact that its values are tabulated in terms of even values of pressure instead of temperature.

As an example of the use of the steam tables, suppose that we wish to determine all of the properties of steam at 120 lb per sq in. pressure and a quality of 0.95. Reference to Table 2 shows that at such a pressure the temperature of evaporation is 341.25° F, which of course is *constant throughout the entire process of evaporation*. Hence 341.25° F is the temperature of the wet vapor under consideration. The specific volume, or cubic feet per pound of steam in this condition, v_x , is strictly given by the sum of the volume of the saturated liquid plus 95% of the volume change of evaporation, i.e.

$$\begin{aligned} v_x &= v_f + xv_{fg} \\ \text{or } v_x &= 0.01789 + 0.95 (3.728 - 0.01789) \\ &= 3.5424 \text{ cu ft.} \end{aligned}$$

Because of the relatively small volume of the saturated liquid the following approximation is entirely adequate for industrial work. The specific volume of evaporation, v_{fg} , represents the difference between v_g and v_f , thus

$$v_{fg} = v_g - v_f$$

Hence the specific volume of a wet vapor may be written

$$\begin{aligned} v_x &= v_f + x(v_g - v_f) \\ &= v_f + xv_g - xv_f \\ &= (1 - x)v_f + xv_g \end{aligned}$$

Since the whole value of v_f is only a small part of v_g and since the above equation shows that only a fraction of it is to be added to xv_g , the quantity $(1 - x)v_f$ is negligibly small. Consequently, we may consider that the specific volume of a wet vapor is given by

$$v_x = xv_g$$

The difference between this approximation and the exact computation given above may be shown as follows

$$\begin{aligned} v_x &= 0.95 \times 3.728 \\ &= 3.5416 \text{ cu ft} \end{aligned}$$

Hence the error resulting from use of the approximate equation is only 0.0008 cu ft.

The first column of the group headed enthalpy gives the change in enthalpy from 32° F to the condition of saturated liquid at the indicated

pressure. The second column gives the change in enthalpy accompanying evaporation at the same pressure. The third column, whose values are the sum of the corresponding values in the first and second columns, gives the total change in enthalpy between the state of saturated steam at the specified pressure and water at 32° F and the same pressure. The value of h for a wet vapor may be determined as follows

$$h_s = h_f + xh_{fg}$$

Then for the particular case under consideration

$$\begin{aligned} h_s &= 312.44 + 0.95 \times 877.9 \\ &= 312.44 + 834.01 = 1146.45 \text{ Btu} \end{aligned}$$

If the specified state was achieved by heating the medium at a constant pressure from 32° F, this value of h_s is the same as the heat required (${}_1Q_2$).

The first and third columns under the heading entropy give the values of the entropy change of one pound of medium between 32° F and the specified state, i.e., saturated liquid and saturated vapor corresponding to the indicated pressure. The second column lists the entropy change resulting from the heat added to produce evaporation under the indicated pressure. Then, since the quality x gives the percentage weight of liquid evaporated, the entropy per pound of wet vapor above 32° F is obtained thus

$$s_s = s_f + xs_{fg}$$

For the illustrative state given

$$\begin{aligned} s_s &= 0.4916 + 0.95 \times 1.0962 \\ &= 0.4916 + 1.0415 = 1.5331 \end{aligned}$$

Intrinsic energy is listed as internal energy in the tables and is designated by u instead of e which we have used in this text. Allowances being made for this difference in notation, the intrinsic energy of a pound of wet vapor above 32° F may be obtained as follows

$$e_s = e_f + xe_{fg} = e_f + x(e_g - e_f)$$

For the state given on page 169

$$\begin{aligned} e_s &= 312.05 + 0.95(1107.6 - 312.05) \\ &= 312.05 + 0.95(795.55) = 312.05 + 755.77 \\ &= 1067.82 \end{aligned}$$

When values of e are not tabulated, this need cause no serious concern. Intrinsic energy per pound (above 32° F) can be readily calculated

from knowledge of the enthalpy, volume, and pressure of any state. The definition of enthalpy is

$$h = e + \frac{pv}{J}$$

Whence

$$e = h - \frac{pv}{J}$$

Thus, values for the intrinsic energy per pound of saturated liquid and saturated vapor may be obtained by direct substitution in the equation of the tabulated values of h_f , p , and v_f for e_f and of h_g , p , and v_g for e_g . In accordance with the definition of enthalpy, the pressure p is always the absolute pressure. Also, in order that the units of the equation may be consistent, the pressure must be expressed in such units that its product with v gives units of work. In the British system this means that pressure *must be expressed in pounds per square foot*.

When the medium is a wet vapor the values of h and v that are substituted in the equation must correspond to the state indicated by the quality. Pressure, however, is *quite independent of quality*. With these stipulations in mind, we are ready to proceed to the determination of e for the wet vapor specified on page 169.

$$e_x = h_x - \frac{pv_x}{J}$$

$$h_x = 312.44 + 0.95 \times 877.9 \quad (\text{page 170})$$

$$= 1146.45 \text{ Btu per lb}$$

$$v_x = 0.95 \times 3.728$$

$$= 3.5416 = 3.54 \text{ cu ft (approx) per lb} \quad (\text{page 169})$$

$$\text{Then } e_x = 1146.45 - \frac{120 \times 144 \times 3.54}{778}$$

$$= 1146.45 - 78.6$$

$$= 1067.85 \text{ Btu per lb}$$

The entire arrangement of Table 3 differs from that of Tables 1 and 2. The reason for this is that when heat is added to a saturated vapor, pressure alone no longer suffices to specify the state. We must know *two* coordinates, as is generally necessary for specifying the state of any medium not undergoing change of phase. When water vapor is heated beyond the saturation point, it is said to be *superheated steam*; Table 3 is used to determine the properties of steam in this condition. The independent variables of the table are pressure and temperature ($^{\circ}\text{F}$). The values of the saturation temperature for corresponding values of pressure are listed for convenience in parentheses under the pressure. The use of Table 3 involves no arithmetic other than simple interpo-

tion For example, the properties per pound of steam at a pressure of 200 lb per sq in. and temperature of 500° F are

$$v = 2.726 \text{ cu ft}$$

$$h = 1268.9 \text{ Btu (above } 32^\circ \text{ F)}$$

$$s = 1.6240 \text{ Btu per } ^\circ \text{F (above } 32^\circ \text{ F)}$$

Sometimes the state of superheated steam is specified by the pressure and the number of degrees temperature *above* the saturation temperature. This temperature interval is called *degrees of superheat*. When the state is specified in this way, it is an easy matter to add the saturation temperature to the given number of degrees of superheat to obtain a value for temperature with which to enter the table.

Physical and Graphic Interpretation of Steam Tables

The physical significance of the values listed in the steam tables may be seen more clearly by graphing the process of warming, evaporating, and superheating water, all at a *constant pressure*, on the pv and TS diagrams (Fig. 5-2). Let us consider the pV diagram first, bearing in mind that by its nature it will yield chiefly information concerning volume changes. Point A represents 1 lb of water at 32° F and at the vapor pressure of water corresponding to that temperature. Likewise point B indicates the state, in terms of p and v , of 1 lb of water at a considerably higher temperature and corresponding pressure, point E , a still higher temperature and pressure. Then the line ABE is the locus of the state points of saturated *liquids* at various pressures. As such, it is conveniently designated the *liquid line* and labeled v_f . When heat is added to a saturated liquid, the liquid begins to evaporate, with an attendant large increase in volume. If evaporation is *not* complete, the state point of the resulting wet vapor is specified by the point x between B and C at a distance from B proportional to the quality. The completion of evaporation for the pressure p_1 is indicated by point C , for a higher pressure, p_2 , by point F . Consequently, the line FGH is the locus of the state points of saturated vapor at various pressures, and so is properly called the *saturation line* (v_g). When steam is heated beyond saturation, it enters the region of superheat, i.e., that area of the diagram in which any state point indicates the superheated condition. The superheating process is accompanied by an increase of the specific volume, as is shown by lines CD and FG for constant pressures p_1 and p_2 respectively.

The TS diagram shows entropy changes for the evaporation process in the same way that the pv diagram shows volume changes. More than that, the area under the curve on the TS diagram that represents

reversible constant-pressure warming, evaporation, and superheating measures the heat added during the change. Under the same condition, change in enthalpy also measures the heat added. Therefore, for the particular condition of reversible constant-pressure change, it is possible to give a graphic representation of h_f , h_{fg} , and h_g .

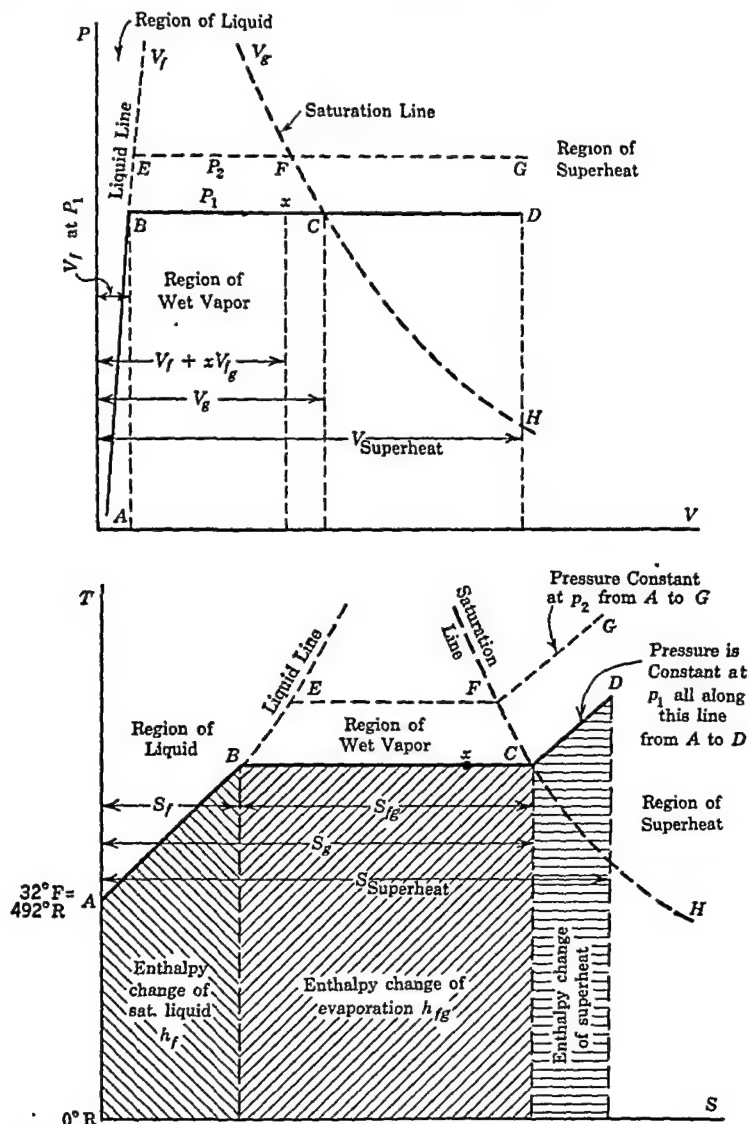


FIG. 5-2. Graphic Representations of the Process of Warming, Evaporating, and Superheating Water at Constant Pressure.

The diagram shows a constant pressure line $ABCD$. Point A represents water at 32°F . As the water is warmed under pressure p_1 , both temperature and entropy increase until the evaporation temperature corresponding to p_1 is reached at point B . The area under AB to the S axis represents the enthalpy h_f above 32°F for the pressure p_1 . At a higher pressure p_2 , the evaporation temperature is higher, and so the warming process continues until point E is reached. Evidently, the line ABE is the locus of the state points of saturated liquid for various pressures. It is therefore the liquid line, and all state points to the left of it indicate that the medium is in the liquid phase.

When heat is added to the saturated liquid, it immediately starts to evaporate. The temperature remains constant until the process is completed, at which time its state point is C . Each point on the line BC therefore represents a state point of wet vapor, as for example, point x . When the evaporation is carried on at a higher pressure p_2 , the condition of saturated vapor is reached at point F . Therefore, the line HCF is the locus of the state points of saturated vapor for various pressures and so is called the saturation line. For the pressure p_1 , the area under BC to the S axis measures the latent heat of evaporation or, what amounts to the same thing, the enthalpy change h_{fg} of evaporation.

It is to be noted that the liquid and saturation lines have opposite slopes. They eventually meet to form a continuous curve, the highest point of which is the critical point (see page 118). Since any state point in the region between the liquid and saturation lines denotes that the medium is a wet vapor, this is called the region of wet vapor.

Further addition of heat after the condition of saturated vapor is reached results in superheating the vapor. Although the process is still carried on at a constant pressure, both temperature and volume increase. The temperature rise accompanying this addition of heat is indicated by the line CD on the TS diagram. Since CD represents a constant pressure process, the area under it indicates the enthalpy change of superheat. The sum of h_f , h_{fg} , and the enthalpy change of superheat is the value of h given in the tables for superheated steam in a state such as D . Any state point to the right of the saturation line indicates that the steam is superheated, hence this area is called the region of superheat. The further the state point of a medium is removed to the right of the saturation line, the more the medium behaves like a gas. Therefore the region of gaseous state points is an extreme extension of the region of superheat.

It is of importance to understand clearly the general trend of the change in the several point functions which accompanies each of the limiting changes of state. For example, it is by no means enough to know only that volume is constant on a constant-volume change. We must also have clearly in mind the change in temperature, pressure,

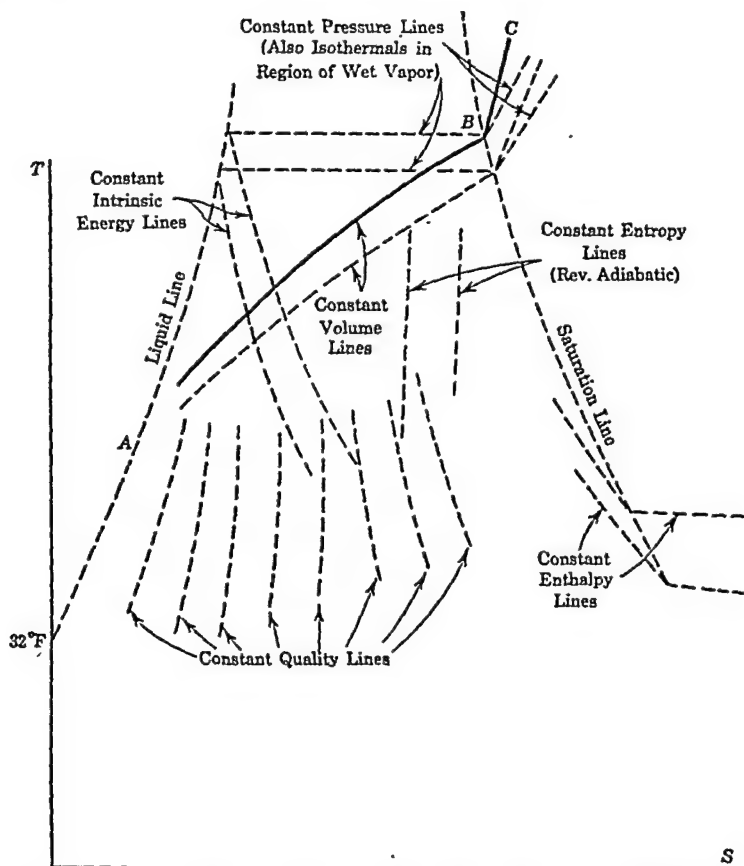


FIG. 5-3. Constant-Volume Change for Water Vapor, Shown on the TS Diagram.

intrinsic energy, enthalpy, and entropy that results from a constant-volume change. Only through such understanding can we proceed to an intelligent determination of ${}_1Q_2$, ${}_1W_2$, and availability of the heat flow of the change. The graphic representation of the limiting changes of state on the TS diagram is an indispensable aid in gaining an understanding of this sort. Thus, the constant-volume line ABC shown on the TS diagram in Fig. 5-3 yields the following information. In the

Non-Flow Constant-Volume Change of State of Water Vapor

For any constant volume change ${}_1W_2$ is zero, and so the Non-Flow Energy Equation for such a change reduces to

$${}_1q_2 = e_2 - e_1 + {}_1W_2]_{-0} \text{ in work units}$$

$$\text{or} \quad {}_1q_2 = \Delta e \text{ in heat units per lb of steam}$$

Thus, the heat flow of the change may be obtained directly from the determination of Δe . The values of e_1 and e_2 for the initial and final states of the steam may be computed from the given value of v and the tabulated values of h for each state respectively. But in order to obtain h for the final state, the coordinates of that state must be known. Usually the final pressure is given, but additional information is required before the state is uniquely specified. For a wet vapor we must also know the quality; for a superheated vapor we must know the temperature. In either case the required data may be obtained from the equation that defines the change, i.e.

$$e_1 = e_2$$

$$\text{So} \quad v_1 e_{g1} = x_2 e_{g2}$$

In case the steam is superheated in either the initial or the final state this becomes

$$e_{\text{superheat 1}} = x_2 e_{g2}$$

$$\text{or} \quad x_1 e_{g1} = e_{\text{superheat 2}}$$

The application of this simple equation is illustrated in the following example. The entropy change that accompanies a constant-volume change of state of a vapor is easily determined once the coordinates of the initial and final states are established. We have then only to determine s_1 and s_2 , taking account of the quality if the vapor is wet or of the temperature if it is superheated. Then directly

$$\Delta s = s_2 - s_1 \text{ per lb} \quad \text{or} \quad \Delta S = M(s_2 - s_1) \text{ for } M \text{ lb of steam}$$

Example

Two lb of steam are cooled at a constant volume of 6.0 cu ft from an initial pressure of 160 lb per sq in. abs to a final pressure of 10 lb per sq in. abs. Find the heat removed and the change in entropy.

Solution

Reference to the saturated steam tables* discloses that the volume of 1 lb of saturated steam at 160 lb per sq in. abs is 2.834 cu ft. Since the initial

* From time to time, the values given in steam tables are revised to a greater degree of accuracy. As a result, there are minor discrepancies in successive editions of the tables. These discrepancies account for small differences that the student may encounter as he checks the solutions given with the tables available for his use.

volume of *one* pound of steam in the tank is 3 cu ft, *it is superheated*. Consequently we enter the superheat tables with pressure of 160 lb per sq in. and find that the properties of steam at such pressure and a volume of 3 cu ft are

$$\begin{aligned}p_1 &= 160 \text{ lb per sq in. abs} \\t_1 &= 400^\circ \text{ F} \\v_1 &= 3 \text{ cu ft per lb} \\h_1 &= 1217.6 \text{ Btu per lb} \\s_1 &= 1.5908 \text{ Btu per } ^\circ \text{ F}\end{aligned}$$

We now must establish the coordinates of the final state. At 10 lb per sq in. abs $v_{g2} = 38.42$ cu ft; hence the steam is wet after the constant-volume cooling. Its quality in the final state is determined by the relation

$$v_1 = v_2 = x_2 v_{g2} = 3 \text{ cu ft per lb}$$

By substituting the tabulated value of v_{g2} , we have

$$\begin{aligned}x_2(38.42) &= 3 \\x_2 &= \frac{3}{38.42} = 0.0781\end{aligned}$$

The properties of the steam in the final state may now be tabulated.

$$\begin{aligned}p_2 &= 10 \text{ lb per sq in. abs} \\t_2 &= 193.21^\circ \text{ F} \\v_2 &= 3 \text{ cu ft per lb} \\h_2 &= h_{f2} + x_2 h_{fg2} = 161.17 + 0.0781 \times 982.1 \\&= 161.17 + 76.70 = 237.87 \text{ Btu per lb} \\s_2 &= s_{f2} + x_2 s_{fg2} = 0.2835 + 0.0781 \times 1.5041 \\&= 0.2835 + 0.1175 = 0.4010 \text{ Btu per } ^\circ \text{ F per lb}\end{aligned}$$

In a constant-volume process

$$\begin{aligned}1Q_2 &= (e_2 - e_1) \text{ or } 1Q_2 = E_2 - E_1 \\E_1 &= M\left(h - \frac{p_1 v_1}{J}\right) = 2\left(1217.6 - \frac{144 \times 160 \times 3}{778}\right) \\E_1 &= 2257.6 \text{ Btu} \\E_2 &= M\left(h_2 - \frac{p_2 v_2}{J}\right) = 2\left(237.87 - \frac{144 \times 10 \times 3}{778}\right) \\E_2 &= 464.7 \text{ Btu}\end{aligned}$$

Then $1Q_2 = 464.7 - 2257.6 = (-)1792.9$ Btu (withdrawn)

The change in entropy for the process and for 2 lb of steam is

$$M(s_2 - s_1) = 2(0.4010 - 1.5908) = (-)2.3796 \text{ Btu per } ^\circ \text{ F}$$

The negative sign indicates a decrease of entropy. This is in accord with the fact that heat is withdrawn from the vapor during the change.

It is impracticable to use the Mollier chart for the solution of this particular problem. True, state 1 may be easily located at the intersection of the 160 lb per sq in. pressure line and the 400° F constant-temperature line (*not* the degree of superheat line). It is then a simple

matter to read the ordinate and abscissa of this state point as h_1 and s_1 respectively. However, the coordinates of state 2 are beyond the range of the chart, and so it cannot be used to determine h_2 and s_2 . It is therefore best to use the tables exclusively for the whole problem.

Non-Flow Constant-Pressure Change of State of Water Vapor

Both the steam tables and the Mollier chart provide a ready means of determining ${}_1q_2$ and Δe for a non-flow constant-pressure change of state of steam. The value of ${}_1q_2$ is given directly by the enthalpy change of the process (see page 85)

Thus ${}_1q_2 = h_2 - h_1$ (per lb of steam)

Since the pressure is known and since the volume in the initial and final states may be obtained from the tables, e_2 and e_1 may be determined by use of the relation

$$e = h - \frac{pv}{J}$$

The evaluation of ${}_1W_2$ is readily accomplished by consideration of the $\int p dv$ with p constant, i.e.

$${}_1W_2 = \int_1^2 p dv = p \int_1^2 dv = p(v_2 - v_1) \text{ ft-lb per lb of steam}$$

The entropy change Δs of the process is determined directly by computing from the tables the values of s_2 and s_1 . Then

$$\Delta s = s_2 - s_1 \text{ (per lb of steam)}$$

It must be kept in mind that h_2 , h_1 , e_2 , e_1 , s_2 , and s_1 refer to the values of these properties in the final and initial states respectively. Either final or initial state or both may be in the region of wet vapor or superheat. Consequently, in solving a problem involving a non-flow constant-pressure change, we must know the coordinates of both initial and final states. The equation of the change, $p = \text{const}$, gives us no help in determining an unknown coordinate, except in the single case where either the initial or the final state is a saturated vapor. The given data must include values of some coordinate of the initial and final states, in addition to the constant pressure at which the change takes place. For example, the data might include the constant pressure, the entropy in the initial state, and the volume in the final state. Let us assume that the process is a constant-pressure increase of volume from an initial state of wet vapor. The state of wet vapor is most conveniently designated by pressure and quality. In this case pressure is already known. Quality may be computed from the given value of entropy by

$$s_2 = s_f + xs_{fg}$$

The value of s_x is the given value of entropy, and the values of s_f and s_{fg} are the tabulated values for the given pressure. With the value of x thus obtained, it is a simple matter to compute the values for all the properties in the initial state. Since we have the volume of the final state, we look first for the tabulated value of saturated steam at the given pressure. Suppose that the given volume is greater than the saturated volume. We know at once that the steam is superheated in the final state. Hence we enter the superheat tables with the given pressure and look across the table until we find the given value of volume. The values of h and s corresponding to it may then be immediately read from the table.

The analysis of the same problem with the Mollier chart is made as follows. The initial state point is located on the chart by finding the point on the given constant-pressure line which has an abscissa equal to the given value of entropy. In order to locate the final state point, however, the tables must be used as previously indicated, because volume is not recorded on the chart. With the state of the superheated steam located in the tables, we may use the value of either entropy or enthalpy given therein to fix the final state point on the given constant-pressure line. The heat added during the change may then be read directly from the chart as the difference in the ordinates of the two state points. Likewise, the entropy change of the medium during the process is given by the difference in the abscissas of the two points.

Example

One lb of steam initially at 150 lb per sq in. abs pressure and quality 0.80 expands at constant pressure. (a) If the process continues until the volume doubles, determine the heat required. (b) How much work is done? (c) What is the temperature at the beginning and end of the expansion? (d) What is the entropy change?

Solution

(a) The initial volume of the steam is ascertained from the equation $v_1 = x_1 v_{g1}$, where v_{g1} is obtained from the saturated steam tables for steam at 150 lb per sq in. abs.

$$\begin{aligned} v_1 &= 0.8 \times 3.015 \\ &= 2.41 \text{ cu ft per lb} \end{aligned}$$

If the volume is doubled, $v_2 = 4.82$ cu ft per lb.

The volume of saturated steam at 150 lb per sq in. abs is 3.015 cu ft per lb. Hence the steam at state point 2 is superheated. For a constant-pressure change

$$\begin{aligned} {}_1Q_2 &= M(h_2 - h_1) \\ h_1 &= h_{f1} + x_1 h_{fg1} \end{aligned}$$

Substituting values from the steam tables for h_f and h_{fg} for steam at 150 lb per sq in abs gives

$$\begin{aligned} h_1 &= 330.51 + 0.8 \times 863.6 \\ &= 1021.39 \text{ Btu per lb} \end{aligned}$$

By entering the superheated steam table with pressure of 150 lb per sq in abs and interpolating for a volume of 4.82 cu ft per lb, we find that h_2 is 1412.9 Btu per lb

$$\begin{aligned} {}_1Q_2 &= 1(1412.9 - 1021.39) \\ &= 391.5 \text{ Btu} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad {}_1W_2 &= p(v_2 - v_1) \\ &= 144 \times 150 \times (4.82 - 2.41) \\ &= 144 \times 150 \times 2.41 \\ &= 52,100 \text{ ft lb} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad &\text{From the saturated steam table, } t_1 = 358.42^\circ \text{ F} \\ &\text{From the superheated steam table, } t_2 = 765^\circ \text{ F} \end{aligned}$$

(d) Since in the initial state the vapor is wet, s_1 is determined by using the values of s_f and s_{fg} for steam at a pressure of 150 lb per sq in abs in the equation

$$\begin{aligned} s_1 &= s_f + x_1 s_{fg} \\ &= 0.5138 + 0.8 \times 1.0556 \\ &= 1.35828 \text{ Btu per } ^\circ \text{ F per lb} \end{aligned}$$

From the superheated steam table for $p = 150$ lb per sq in abs and a volume of 4.8234 cu ft per lb

$$\begin{aligned} s_2 &= 1.7822 \text{ Btu per } ^\circ \text{ F per lb} \\ \Delta s &= 1.7822 - 1.35828 = 0.4239 \text{ Btu per } ^\circ \text{ F per lb} \end{aligned}$$

Parts (a) and (d) of this example may also be quickly solved with the Mollier diagram. Interpolate a 150 lb per sq in constant pressure line between the ones given on the chart for 140 and 160 lb per sq in. The intersection of this line with the constant moisture percentage line (moisture percentage = 1.00 - quality) labeled 20 gives the initial state point. The ordinate of this point is $h = 1022$ Btu and the abscissa is $s_1 = 1.359$ Btu per $^\circ \text{ F}$. As previously mentioned, the final state must be located in the superheat tables, because it is specified by the volume. The temperature in the final state is then obtained as 770.6° F . Interpolate a constant temperature line of this value between those given on the chart for 740° F and 780° F . Its intersection with the 150 lb per sq in pressure line fixes the final state point, of which the ordinate and abscissa are respectively $h_2 = 1414$ Btu per lb and $s_2 = 1.786$. When the values of h_1 , h_2 , s_1 , and s_2 obtained from the chart are compared with those obtained from computations with the tables, it is seen that the *percentage* error resulting from the use of even a small scale is not great.

Non-Flow Isothermal Change of State of Water Vapor

The determination of ${}_1Q_2$, ΔE , and ${}_1W_2$ for a non flow isothermal change of state of steam gives considerable insight into the application of fundamental principles. First we must realize that when the medium

is a vapor, ΔE is not zero as it is for the non-flow isothermal change of a perfect gas. Also, the equation of the change is radically different from $pV = \text{const.}$ In fact, the best we can do to express the equation of the change is to write $T = \text{const.}$ Hence, in general we do not know the relation between p and v for the change and so cannot compute ${}_1W_2$ from $\int p dV$. One principle we can use, however, if the change is reversible as well as isothermal, is that

$${}_1Q_2 = \int T dS$$

and since T is constant

$${}_1Q_2 = T(S_2 - S_1) = MT(s_2 - s_1)$$

From specification of the initial and final state points we may compute s_2 and s_1 from the tables and substitute to obtain ${}_1Q_2$. Values of e_2 and e_1 may also be computed from the tables by

$$e = h - \frac{pv}{J}$$

Then

$$\Delta E = E_2 - E_1 = M(e_2 - e_1)$$

With both ${}_1Q_2$ and ΔE known, it is easy to substitute in the Non-Flow Energy Equation and obtain ${}_1W_2$, thus

$${}_1Q_2 = \Delta E + \frac{{}_1W_2}{J} \text{ (in heat units)}$$

or

$${}_1W_2 = JM({}_1q_2 - \Delta e)$$

When both initial and final state points are in the region of wet vapor, there is no necessity for using this analysis. *For a wet vapor, pressure is a function of temperature only. Consequently, an isothermal change in the region of wet vapor is also a constant-pressure change and should be treated as such.* If the steam is superheated in either the initial or the final state, this simplification is no longer possible, for in the region of superheat temperature is a function of both pressure and volume. Under such circumstances the analysis in the preceding paragraph must be used.

Example

One lb of superheated steam initially at 100 lb per sq in. abs and 400° F is compressed isothermally and reversibly to the state of a saturated vapor. It is then condensed isothermally until its quality becomes 0.35. Determine (a) the pressure of the saturated vapor; (b) the entropy change, heat flow, change in intrinsic energy, and the work done (1) for the isothermal compression, (2) for the isothermal condensation.

Solution

It will help in understanding the nature of this process to refer to its graphic representation on the TS plane, shown in Fig. 5-5

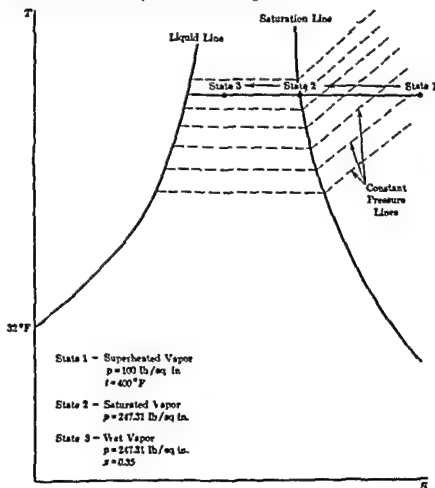


FIG. 5-5

(a) The pressure of a saturated vapor corresponding to a temperature of saturation of 400°F is read directly from the saturated steam tables

$$p_2 = 247.31 \text{ lb per sq in. abs}$$

(b-1)

$$s_1 = 1.6518 \text{ Btu per } ^\circ \text{F per lb}$$

$$s_2 = 1.5272 \text{ Btu per } ^\circ \text{F per lb}$$

$$\Delta s = s_2 - s_1 = (-) 0.1246 \text{ Btu per } ^\circ \text{F per lb}$$

In order to find ${}_1q_2$, ${}_1W_2$ and $e_2 - e_1$ we must rely on the energy equation for a non flow process, and evaluate the terms therein by the best means available

$$J_1q_2 = e_2 - e_1 + {}_1W_2$$

Since this is an isothermal reversible process

$$\Delta s = \frac{q_2}{T}$$

and

$$\begin{aligned} {}_1q_2 &= T \Delta s \\ &= (400 + 460)[(-) 0.1246] \\ &= -(860 \times 0.1246) = (-) 107 \text{ Btu per lb (heat withdrawn from medium)} \end{aligned}$$

For the determination of $e_2 - e_1$ we again use the equation

$$e = h - \frac{pv}{J}$$

or

$$\begin{aligned} e &= Jh - pv \text{ (in work units)} \\ e_2 - e_1 &= J(h_2 - h_1) + (p_1v_1 - p_2v_2) \\ &= 778(1201 - 1227.6) + 144(100 \times 4.937 - 247.31 \times 1.8633) \\ &= 778(-26.6) + 144(33.7) \\ &= -20,700 + 4320 \\ &= (-) 16,380 \text{ ft-lb per lb (a decrease)} \end{aligned}$$

Substituting in the Non-Flow Energy Equation gives

$$\begin{aligned} (-) 778 \times 107 &= (-) 16,380 + {}_1W_2 \\ {}_1W_2 &= -83,250 + 16,380 \\ {}_1W_2 &= (-) 66,870 \text{ ft-lb per lb (work of compression)} \end{aligned}$$

(b-2) The condensation process is both isothermal and constant pressure.

$$s_2 = 1.5272 \text{ (entropy of the saturated vapor at } 400^\circ \text{ F)}$$

$$s_3 = s_{f3} + x_3 s_{fg3}$$

For the state specified by $T_3 = 400^\circ \text{ F}$, $p_3 = 247.31$, and $x_3 = 0.35$

$$\begin{aligned} s_3 &= 0.5664 + 0.35 \times 0.9608 \\ &= 0.9004 \\ s_3 - s_2 &= 0.9004 - 1.5272 \\ &= (-) 0.6268 \text{ Btu per } ^\circ \text{F per lb} \\ {}_2q_3 &= h_3 - h_2 \text{ (constant-pressure process)} \\ h_2 &= 1201.0 \text{ Btu per lb} \\ h_3 &= h_{f3} + x_3 h_{fg3} \\ &= 374.97 + 0.35 \times 826.0 \\ &= 664 \text{ Btu per lb} \\ {}_2q_3 &= 664.0 - 1201.0 = (-) 537.0 \text{ Btu per lb} \\ {}_2W_3 &= p(v_3 - v_2) \\ v_2 &= 1.8633 \text{ cu ft per lb} \\ v_3 &= 0.35(v_{g3}) = 0.35 \times 1.8633 \text{ cu ft per lb} \\ {}_2W_3 &= 144 \times 247.31 \times 1.8633(0.35 - 1) \\ &= (-) 43,150 \text{ ft-lb per lb} \end{aligned}$$

We may obtain the value of $e_3 - e_2$ from substitution in

$$\begin{aligned} J{}_2q_3 &= e_3 - e_2 + {}_2W_3 \\ (-) 778 \times 537 &= e_3 - e_2 - 43,150 \\ e_3 - e_2 &= (-) 418,000 + 43,150 \\ &= (-) 374,850 \text{ ft-lb per lb} \end{aligned}$$

It is suggested that the student check the solution of this example by means of the Mollier chart, so far as the range of the chart permits.

Non Flow Adiabatic Change of State of Water Vapor

In the study of the Carnot cycle we learned that the non flow reversible adiabatic change is the most effective path for the passage of the medium from the high to the low temperature of a heat utilizing cycle. As such it is often established as the standard with which the expansion in an actual engine is compared. As previously discussed (page 72) a reversible adiabatic change is isentropic and so the equation that defines it is

$$s = \text{const}$$

When one state of a medium undergoing reversible adiabatic change is known this equation makes possible the fixing of the second state from knowledge of only one of its coordinates. For example, when saturated steam expands reversibly and adiabatically from p_1 to p_2 the quality in the second state is obtained from

$$s_1 = s_2$$

In this case $s_1 = s_g$ at pressure p_1 and $s_2 = s_f + x s_{fg}$ at pressure p_2 . Then $s_{g1} = s_{f2} + x s_{fg2}$ in which all quantities except x are available in the tables. The same procedure is valid if either the initial or the final state points are in the region of wet vapor, at saturation, or in the region of superheat.

The Non Flow Energy Equation for a reversible adiabatic change reduces to

$$0 = \Delta E + {}_1H_2$$

$$\text{or } {}_1H_2 = -\Delta E = -M(e_2 - e_1) = M(e_1 - e_2) \text{ (in work units)}$$

The values of e_1 and e_2 are computed from values for h , p and v in each state as previously described. Their difference $e_2 - e_1$ with proper attention paid to units gives the negative of ${}_1H_2$ directly.

The Mollier chart is particularly well adapted to the study of a reversible adiabatic change. Its application is described in the following example.

Example

Steam at 200 lb per sq in. abs pressure and 48.18° of superheat enters a reciprocating steam engine cylinder and expands to a pressure of 90 lb per sq in. abs adiabatically and reversibly. How much work is ideally performed per pound of steam?

Solution

$$\begin{aligned} {}_1H_2 &= -(e_2 - e_1) = e_1 - e_2 \\ e &= (Jh - pv) \text{ (in work units)} \\ {}_1H_2 &= J(h_1 - h_2) + (p_2 v_2 - p_1 v_1) \end{aligned}$$

It then becomes necessary to determine h and v for both initial and final states of the steam. In the initial condition the steam is at 200 lb per sq in. abs

of a vapor in the same way as that of a gas, i.e., by the equation $pV^n = \text{const}$. As previously described (page 39), the value of n is determined from experimental measurement of p and V for two of the state points of the particular change under consideration. Let us emphasize that when the medium is a vapor a polytropic change may be designated by a variety of values of n which will usually lie in the neighborhood of 1.

Unlike the case when the medium is a gas, equations in T and p and T and V cannot be conveniently written. For a gas both of these relationships were obtained by combining $pV^n = \text{const}$ with the characteristic equation for gas. The characteristic equation for water vapor is far different from the simple gas equation, and any equation formed by combining $pV^n = \text{const}$ with it would be of baffling complexity. Consequently, if the given data of a problem in the polytropic change of a vapor fix the state with coordinates other than p and V , we must use the given facts to establish values of three of the four quantities p_1 , V_1 , p_2 , and V_2 . The equation then provides an easy means of determining the fourth quantity. Ordinarily we can measure pressures and volumes more easily than any other coordinates. This being the case, with the value of n known, we may apply the equation at once to obtain one unknown value of p and V in the initial or final state.

The most directly determinable quantity in the Non Flow Energy Equation for a polytropic change is ${}_1W_2$. This is given by the integration of $\int p dV$ over the particular path specified by the value of n in $pV^n = \text{const}$. We have already done this integration (pages 45-46) with the following result:

- (a) When $n = 1$, which designates a polytropic, *not* an isothermal change of a vapor

$${}_1W_2 = p_1 V_1 \log_e \frac{V_2}{V_1}$$

- (b) When n has any finite value other than 1

$${}_1W_2 = \frac{p_2 V_2 - p_1 V_1}{1 - n}$$

The fixing of the initial and final state points of the change makes it possible to obtain all of the properties of the vapor in those states. From this information it is possible to calculate E_1 , E_2 , and hence ΔE as before from the relation

$$e = \left(h - \frac{pv}{J} \right)$$

$$\text{or} \quad E = M \left(h - \frac{pv}{J} \right) \text{ (in heat units)}$$

$$\text{or} \quad E = M(Jh - pv) \text{ (in work units)}$$

Then, with the aid of the Non-Flow Energy Equation, we obtain the value of ${}_1Q_2$ from the computed values of ΔE and ${}_1W_2$ for the change, i.e.

$${}_1Q_2 = \Delta E + {}_1W_2 \text{ (in work units)}$$

or
$${}_1Q_2 = \Delta E + \frac{{}_1W_2}{J} \text{ (in heat units)}$$

The tabulation of the properties of the steam in its initial and final state points includes values for s_1 and s_2 . The simple difference between these two values is the entropy change of the process per pound of vapor. If M lb of vapor are involved in the change, ΔS is given by

$$\Delta S = M(s_2 - s_1)$$

Usually there is no advantage in using the Mollier chart for the analysis of a polytropic change. There is no representation of volume on the chart and since the initial and final states of a polytropic change must eventually be specified in terms of pressures and volumes, the tables must be used in any event. This being the case, it is really easier to use them exclusively for the entire problem.

Example

Steam having an initial quality of 0.90 at 80 lb per sq in. abs expands in a cylinder until the pressure is 14 lb per sq in. abs. The equation of the path is $pV = \text{const}$, i.e. ($n = 1$ in the path equation $pV^n = \text{const}$). Determine, per pound of steam, (a) initial and final volume of the steam, (b) the entropy change of the steam, (c) the work done, (d) the change in intrinsic energy, (e) the heat flow.

Solution

(Notice carefully that the equation $pv = \text{const}$ denotes a polytropic change of a vapor.)

$$\begin{aligned} \text{(a)} \quad v_1 &= x_1 v_{g1} \\ &= 0.9 \times 5.472 = 4.9248 \text{ cu ft per lb} \end{aligned}$$

To find v_2 it is necessary to use the equation of the path, i.e., $pv = \text{const}$.

$$\begin{aligned} p_1 v_1 &= p_2 v_2 \\ v_2 &= \frac{p_1 v_1}{p_2} \\ &= \frac{80 \times 4.9248}{14} = 28.1 \text{ cu ft per lb} \end{aligned}$$

(b) Entropy of the initial state

$$\begin{aligned} s_1 &= s_{f1} + x_1 s_{fg1} \\ &= 0.4531 + 0.9 \times 1.1676 \\ &= 1.504 \end{aligned}$$

Entropy of the final state

$$s_2 = s_{f2} + x_2 s_{fg2}$$

The quality in the final state may be obtained from the ratio of v_2 to the saturation volume at p_2 , thus

$$x_2 = \frac{v_2}{v_{g2}} = \frac{28.1}{28.04} = 1.0$$

From this we see that the steam is a saturated vapor at state 2

$$\begin{aligned} \text{Then } s_2 &= s_{g2} = 1.7604 \\ \Delta s &= s_2 - s_1 = 1.7604 - 1.5040 \\ &= +0.2564 \text{ Btu per } ^\circ\text{R per lb} \end{aligned}$$

$$(c) \quad {}_1W_2 = \int_1^2 p dV, \text{ and for the path given and per pound of steam}$$

$$p = \frac{\text{const}}{v} = \frac{p_1 v_1}{v}$$

$${}_1W_2 = p_1 v_1 \int_1^2 \frac{dv}{v} = p_1 v_1 \log_e \frac{v_2}{v_1}$$

$$\begin{aligned} {}_1W_2 &= 144 \times 80 \times 4.9248 \log_e \frac{28.1}{4.9248} \\ &= 144 \times 80 \times 4.9248 \times 1.7415 \\ &= 99,000 \text{ ft lb per lb} \end{aligned}$$

$$\begin{aligned} (d) \quad e_2 - e_1 &= [J(h_2 - h_1) + (p_2 v_2 - p_1 v_1)] \\ &= 778(1149.3 - 1092.3) + 0 \\ &= 778(57) \\ &= 44,350 \text{ ft lb per lb} \end{aligned}$$

$$\begin{aligned} (e) \quad J_1 q_2 &= e_2 - e_1 + {}_1W_2 \\ {}_1q_2 &= \frac{44,350 + 99,000}{778} = \frac{143,350}{778} \\ &= +184 \text{ Btu per lb} \end{aligned}$$

Constant Enthalpy Change of State of Water Vapor (Throttling Process)

All energy transforming machinery must be provided with suitable controlling apparatus for starting and stopping. This apparatus must also be capable of controlling the operating speed if the load applied to the machinery is not constant. In heat utilizing cycles, both of these objectives are commonly attained by the use of a throttle valve which regulates the quantity of medium admitted to the cycle. A throttle valve is essentially a frictional mechanism which controls the flow of the medium past it by introducing a resistance to flow that may be varied at will. As a result, pressure is always reduced by passage through the throttle. A certain amount of high-grade intrinsic energy in the medium is used to overcome the frictional resistance and is thereby transformed into low grade heat energy. In most cases, the throttling process is nearly adiabatic, so that all of this energy remains in the system. Its availability, however, has been considerably decreased.

The inevitable conclusion is that the use of a throttle valve for speed control confers flexibility at the cost of efficiency. It is therefore desirable to be able to determine precisely the amount of the change of all the thermodynamic quantities involved in a throttling change of state.

In the study of the Joule-Thomson effect we learned that an adiabatic throttling change takes place at constant enthalpy (page 132). The equation that defines the change is

$$h_1 = h_2$$

This relation makes possible the determination of one unknown coordinate for one of the end states of the change. For example, h_1 is readily determined from the tables from knowledge of pressures and quality if the medium is initially a wet vapor. If the steam is initially superheated, pressure and temperature must be given either directly or indirectly. Then, if the pressure at the end of the throttling expansion is given, as is usually the case, the second state is fixed by p_2 and the constant value of enthalpy.

The throttling process is essentially a *flow process*. No external work is done during it and we assume the ideal case to be adiabatic. Hence ${}_1Q_2$ and ${}_1W_2$ are each zero. There is a change in intrinsic energy during the process which may be calculated by determining E_1 and E_2 from the tables with the equation

$$e = h - \frac{pv}{J} \text{ (per lb of steam)}$$

The two major items of interest in a throttling process are (1) the decrease in availability which accompanies the process, and (2) the physical characteristics of the vapor after throttling. So far as the first item is concerned, once the initial and final states are fixed, the values of s_1 and s_2 may be computed from the tables or read directly from the Mollier chart. The product of $(s_2 - s_1)$ times the lowest available absolute temperature then gives the amount of energy rendered unavailable by the process. In connection with the second item, reference to the Mollier chart shows that, except at very high initial pressures, quality *increases* during a throttling change. In fact, for initial states in the neighborhood of the saturation line, the steam may become superheated as its pressure is reduced by throttling. We shall refer to this property of the change in connection with the throttling calorimeter, described in the next section. It may seem an anomaly that, at one and the same time, availability *decreases* and quality *increases*. The fact is that during a throttling change the temperature decreases on the whole and hence availability decreases. But the same total amount of energy

remains in the system. It takes less energy to saturate a vapor at a low pressure than at a high pressure. Therefore, if the total energy in the system remains constant, a saturated vapor becomes superheated as its pressure is reduced even though the temperature also decreases. These ideas are well illustrated by tracing a constant h expansion line on the Mollier chart.

Example

Steam in a main line at 200 lb per sq in. abs and quality 0.98 is throttled or 'wiredrawn' to a pressure of 80 lb per sq in. abs by passage through a partially closed valve. What is the quality of the steam after throttling? What is the change in entropy and the unavailable energy per pound of steam, assuming a condenser temperature of 100° F?

Solution

For a throttling process h is constant. Therefore

$$h_1 = h_2$$

$$h_{f1} + x_1 h_{fg1} = h_{f2} + x_2 h_{fg2}$$

For an initial pressure of 200 lb per sq in. and quality of 0.98 and a final pressure of 80 lb per sq in.

$$355.36 + 0.98 \times 843.0 = 282.02 + x_2(901.1)$$

$$x_2 = \frac{355.36 + 826.14 - 282.06}{901.1} = 0.9982$$

It will be observed that throttling has caused the steam to become practically saturated. Had the final pressure been slightly lower the final state would have been that of superheated steam.

With the Mollier chart, determination of x_2 is quite simple. State point 1 is established at the intersection of the 200 lb per sq in. pressure line and the 0.98 quality line. The constant h line is then followed to its intersection with the 80 lb per sq in. pressure line, at which point x_2 may be read from the chart. The values of s_1 and s_2 may also be read directly from it as the respective abscissas of state points 1 and 2. When the tables are used, s_1 and s_2 are computed as follows:

$$s_1 = s_{f1} + x_1 s_{fg1}$$

$$= 0.5435 + 0.98(1.0018)$$

$$s_2 = s_{f2} + x_2 s_{fg2}$$

$$= 0.4531 + 0.9982(1.1676)$$

$$= 1.618578$$

$$s_2 - s_1 = 0.0933 \text{ Btu per } ^\circ\text{F per lb (increase)}$$

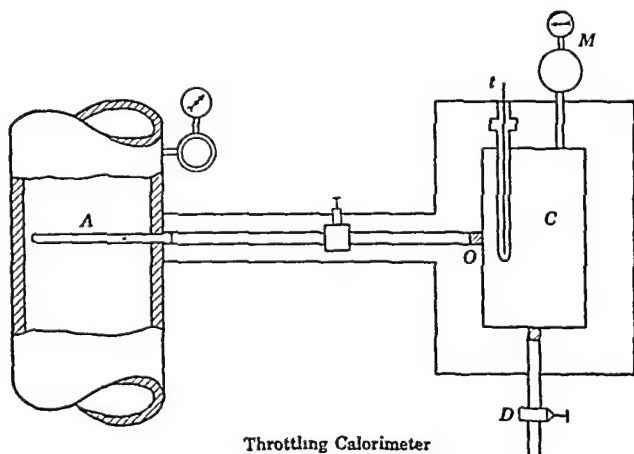
The change in unavailable energy is equal to Δs times the absolute condenser temperature. Therefore

$$Q = (\Delta s)T_0$$

$$= 0.0933 \times 560 = 52.25 \text{ Btu per lb (increase in unavailable energy)}$$

The Throttling Calorimeter

The foregoing example shows that whenever we are dealing with a wet vapor we must have enough data to determine its quality. Actually, quality is readily determined experimentally. An apparatus often used for this purpose is the throttling calorimeter, which depends for its operation on the drying action of the throttling process. A schematic representation of this apparatus is shown in Fig. 5-6. A small sample of



Throttling Calorimeter

FIG. 5-6.

steam is withdrawn from a vertical section of the main steam line through the perforated pipe *A*. The steam expands into the chamber *C* by a throttling process through an orifice *O* to a pressure slightly above atmospheric. The chamber is fitted with a thermometer *t*, and a manometer or gage *M*, which measure respectively the temperature and gage pressure of the steam after expansion. The steam then passes to the atmosphere through the discharge valve *D*.

If the steam is superheated as a result of the expansion, the recorded pressure and temperature in the calorimeter immediately define its state. The initial pressure of the wet steam in the line is readily measured with a gage. Then, since *h* is constant for the throttling process in the calorimeter, the quality of the high-pressure steam may be computed from

$$h_1 = h_2$$

$$h_{f1} + x_1 h_{fg1} = h_2$$

Values of h_{f1} and h_{fg1} are obtained from the tables for saturated steam at the pressure in the line. The value of h_2 is obtained from the tables

for superheated steam for the pressure and temperature in the calorimeter. This leaves x_1 as the only unknown quantity in the equation.

Example

A sample of steam at a pressure of 200 lb per sq in. abs is withdrawn from a main steam line and admitted to a throttling calorimeter in which the pressure is 14.696 lb per sq in. abs. The temperature in the calorimeter is observed to be 290° F. What is the quality of the steam in the line?

Solution

From the given data of the second state, we determine the value of enthalpy h_2 . Inspection of the saturation tables shows that at 14.696 lb per sq in. abs the value of h_g is 1150.4 Btu per lb, and the superheat tables give the value of h_{300° as 1192.8 Btu per lb. The saturation temperature at this pressure is 212° F, hence the temperature interval to 300° F is 88° F. Then by ordinary interpolation methods

$$\begin{aligned} h_2 &= h_{290^\circ} = 1150.4 + \frac{78}{88}(1192.8 - 1150.4) \\ &= 1150.4 + 37.6 \\ &= 1188.0 \text{ Btu per lb} \end{aligned}$$

For the initial state of wet steam at 200 lb per sq in. abs, enthalpy is obtained from

$$\begin{aligned} h_1 &= h_{f1} + x_1 h_{fg1} \\ &= 355.36 + x_1(843.0) \end{aligned}$$

Then, since $h_1 = h_2$

$$\begin{aligned} 355.36 + x_1(843.0) &= 1188.0 \\ x_1 &= \frac{832.6}{843.0} = 0.987 \end{aligned}$$

An easier and quicker solution of the problem can be made by means of the Mollier chart. Locate state point 2 on the chart at the intersection of the 14.696 lb per sq in. pressure line and the 290° F temperature line. Trace a horizontal (constant h) line to its intersection with the pressure line (200 lb per sq in.) of the initial condition of the steam. The point of intersection is state point 1, for which the moisture is read directly from the chart as 1%. The initial quality is therefore $(1 - 0.01) = 0.99$.

Limitations of the Throttling Calorimeter

The use of the throttling calorimeter for the measurement of quality is subject to two limitations. First, great care must be exercised in obtaining a representative sample of steam from the main line. It is to meet this condition that the American Society of Mechanical Engineers recommends that (1) the sample should always be taken from a vertical steam pipe, (2) the intake should be through a so-called calorimeter nipple made of $\frac{1}{2}$ -in. pipe and extending into the steam pipe to a point within $\frac{1}{2}$ in. of the opposite wall, (3) the end of the nipple should be plugged so that the steam must enter through not less than 20 equally

spaced $\frac{1}{8}$ -in. holes. To make the throttling process as nearly adiabatic as possible, the Society recommends that the connection between steam pipe and calorimeter be as short as possible and that all external parts of the calorimeter be well insulated with hair felt.

The second limitation on the use of the throttling calorimeter comes from experiments which show that quality measurements made with it are reliable *only when the expanded steam has at least 10° of superheat*. Usually it is not convenient to expand the steam to a pressure below that of the surrounding atmosphere. Consequently, the amount of moisture that can be determined accurately depends upon the pressure. If we trace a constant h line on the Mollier diagram from a state point at atmospheric pressure and 10° of superheat, we see that if the pressure in the main steam line is 50 lb per sq in. abs, the greatest moisture that can be measured is 2%; if the line pressure is 100 lb per sq in. abs, the greatest moisture that can be measured is 3.5%, and so on.

When the moisture content in the main steam line exceeds that which can be measured with the throttling calorimeter, the separating calorimeter or the barrel calorimeter is used. The first operates by separating the water from the steam by abrupt change in direction and reduction of the velocity of the steam. Because the density of the liquid is many times that of the vapor, the moisture falls to the bottom of the vessel where its amount is measured with a calibrated gage glass. The barrel calorimeter consists simply of a barrel partially filled with cold water. The initial weight of the barrel and its contents is carefully measured, as is also the temperature of the water. Steam is then introduced into the water through a pipe extending nearly to the bottom of the barrel. The steam condenses and thereby raises the temperature of the water. After an appropriate sample of the steam has been thus condensed and temperature equilibrium achieved by thorough stirring, the barrel and its contents are again weighed and the temperature of the water noted. The heat given up by the condensation of the steam is equal to that gained by the water, i.e.

$$Mx_1h_{f01} + M(t_f - t_2) = M_1(t_2 - t_1)$$

in which

M = weight of wet steam introduced (difference in initial and final weights)

M_1 = weight of cold water

t_f = saturation temperature at initial pressure

t_1 = initial temperature of cold water

t_2 = final temperature of water after steam has been condensed in it

h_{f01} = latent heat of evaporation at t_f

All of these quantities may be measured or determined from the steam tables. Hence the equation may be readily solved for x_1

$$x_1 = \frac{M_1(t_2 - t_1) - M(t_f - t_2)}{\Delta h_{f,1}}$$

The student will find it profitable to gather together the various formulas for non-flow water-vapor change of state and enter them in the indicated spaces in Table 5-1

PROBLEMS

- 1 State the practical applications of the Clapeyron and Clausius Clapeyron Equations
- 2 State units for each term of the Clapeyron Equation $\frac{dp}{dT} = \frac{JL}{T(t_2 - t_1)}$ so that a consistent system of units for the equation will result
- 3 What is the boiling point of water at an elevation where the average barometer reading is 622 mm? The normal boiling point at 760 mm is 100° C, and the heat of vaporization at this temperature is 538 cal per g
- 4 The heat of vaporization of water at its boiling point, 100° C at 760 mm, is 538 cal per g. By means of the Clausius-Clapeyron Equation calculate the vapor pressure of water at 54.5° C. If the experimental value is 150 mm, calculate the percentage error
- 5 The vapor pressure of benzene (C_6H_6) is 548 mm at 70° C and 755 mm at 80° C. (a) Calculate the quantity of heat required to vaporize a gram of benzene (b) Calculate the vapor pressure of benzene at 90° C
- 6 The melting point of monoclinic sulphur is 100° C and it increases 0.05° C per atm. The density of monoclinic sulphur is 1.960 and its heat of fusion is 320 cal per at wt. Calculate the density of the liquid by the Clapeyron Equation
- 7 Show on a TS diagram the process of warming, evaporating, and superheating a vapor at constant pressure. Indicate liquid line, saturation line, region of liquid, region of wet mixture, and region of superheat. Also designate the area representing enthalpy of liquid, enthalpy of evaporation, and enthalpy of superheat
- 8 Define saturated liquid, saturated vapor, superheated vapor, saturation temperature, saturation pressure
- 9 What are the coordinates of a Mollier chart? Sketch a Mollier chart indicating the approximate trend of the various lines usually represented thereon
- 10 What is meant by thermodynamic coordinates, and what coordinates may be used to specify the state of (a) a gas, (b) a saturated vapor, (c) a wet vapor, (d) a superheated vapor?
- 11 a Why are the various properties of vapors not easily determinable from mathematical equations?
b What means is available for readily ascertaining the properties of saturated liquids and vapors?

- c List the properties, and the symbols used to identify them which are found in (1) the saturated steam tables, (2) the superheated steam tables
- 12 Define wet vapor Describe the procedure for ascertaining each of the properties of a wet vapor
- 13 How many coordinates are generally required to determine the state of a medium? How many for a saturated vapor? In the saturated steam tables find the properties of 150 lb per sq in abs steam, of quality 0.9
- 14 a What is the quality of saturated vapor? How does quality vary with adiabatic change? How does quality vary with throttling change?
 b Using a Mollier chart, find the quality of steam which has expanded adiabatically and reversibly from a pressure of 50 lb per sq in abs and quality of 0.98 to a pressure of 10 lb per sq in abs
 c Find the quality of steam which has been throttled at constant enthalpy from the same initial state to the same final pressure as above
- 15 One lb of water vapor at 35 lb per sq in abs pressure has a volume of 9.264 cu ft Determine (a) its quality, (b) its temperature, (c) its entropy, (d) its intrinsic energy, (e) its enthalpy h
- 16 One lb of steam is at an absolute pressure of 100 lb per sq in and a temperature of 500° F (a) Is this steam wet, saturated, or superheated? (b) Determine (1) its enthalpy, (2) its entropy, (3) its volume, (4) its intrinsic energy
- 17 In the following types of non flow changes of state of a vapor, what property change measures the energy added or abstracted as heat? (a) constant volume change (b) constant pressure change
- 18 What coordinate is constant during a reversible adiabatic change? What property change measures the work done in a non flow reversible adiabatic change?
- 19 Discuss the characteristics of an irreversible adiabatic change, a throttling process
- 20 Describe the throttling calorimeter, state its principles of operation, and discuss its limitations
- 21 Two lb of dry saturated steam at 250 lb per sq in abs pressure expand reversibly and adiabatically to 12 lb per sq in abs (a) Determine the final quality (use the Mollier chart) (b) Determine the work done
- 22 A minimum of 10° of superheat must be obtained in a throttling calorimeter to give an accurate measure of the quality of the steam admitted to it If the calorimeter pressure remains atmospheric, determine for several pressures the limiting amount of moisture that can be determined with the calorimeter and sketch a curve with P and x as coordinates to show the range of its applicability
- 23 One lb of steam having a pressure of 200 lb per sq in abs has a total entropy of 1.5400 (a) What is the total entropy of dry and saturated steam under the given pressure? (b) Is the steam wet or dry? (c) What is its quality?
- 24 A closed tank containing dry and saturated steam at 15 lb per sq in abs pressure is submerged in a body of water at a temperature of 60° F What will be the ultimate pressure and quality of the steam within the tank?

25. What will be the final enthalpy of dry saturated steam that is expanded adiabatically and reversibly from 150 lb per sq in. abs to 10 lb per sq in. abs?
26. Compute the external work done during the heating of 1 lb of water from 32° F to a saturated vapor at a pressure of 300 lb per sq in. abs. Compare this with the heat which must be supplied.
27. One lb of steam at a pressure of 100 lb per sq in. abs has a volume of 4 cu ft and expands adiabatically and reversibly to 14.696 lb per sq in. abs. (a) What are the qualities at the initial and final conditions? (b) What is the work done during the expansion?
28. One lb of steam at 100 lb per sq in. abs and 50% dry expands at a constant pressure. What work is done and what heat is required to double the volume? What is the temperature at the beginning and end of the expansion?
29. Dry (saturated) steam at 100 lb per sq in. abs pressure contained in a closed tank is cooled until its pressure drops to 14.696 lb per sq in. abs. What is the final quality and the heat removed from each pound of steam?
30. One lb of steam at 100 lb per sq in. abs has a quality of 0.98. It expands along an $n = 1$ curve (i.e., $n = 1$ in $pv^n = \text{const}$) to a pressure of 14.696 lb per sq in. abs. (a) What is the volume at the beginning and end of the expansion? (b) What is the quality at the end of the expansion? (c) How much work is done during the expansion? (d) How much heat must be supplied?
31. Determine the final quality of the steam and find the quantity of work performed by 2 lb of it in expanding reversibly and adiabatically from 250 lb per sq in. abs pressure to 100 lb per sq in. abs, the steam being initially dry and saturated.
32. Steam at 150 lb per sq in. abs has a quality of 0.90. (a) What is the entropy of the liquid? (b) What is the entropy of evaporation? (c) What is the total entropy of the steam?
33. In a boiler, water is vaporized under a constant pressure of 150 lb per sq in. abs. The volume of 1 lb of the steam formed is 3.02 cu ft; the volume of 1 lb of water (sat liquid) is 0.018 cu ft. Find the heat required to perform the work of expansion against the constant pressure.
34. One lb of steam at a pressure of 150 lb per sq in. abs has a quality of 0.73. What work is done and what heat is required to double its volume at constant pressure?
35. In the throttling calorimeter the quality of steam is determined by permitting it to expand (i.e., throttling it) at a constant enthalpy. Steam enters the calorimeter at 160 lb per sq in. abs and is throttled to atmospheric pressure in which state its temperature is 300° F. (a) Determine the quality of the original steam. (b) Check the result by the Mollier chart. (c) State briefly or indicate by diagram the method of determination by the Mollier chart.
36. One lb of steam at 100 lb per sq in. abs and a temperature of 450° F expands adiabatically and reversibly to atmospheric pressure. (a) Determine its enthalpy, entropy, quality, volume, temperature, and intrinsic energy in the final state. (b) Determine the work done during the expansion.

Compressed Air

The Use of Compressed Air

Until now, we have been concerned with the study of energy transformations and the availability of heat energy. The object has been to gain a clear understanding of the principles which underlie the operation of any process for the transformation of the energy of natural resources into industrial power. In this and in subsequent chapters we shall consider the application of these fundamental principles to some processes and cycles encountered in engineering practice.

We shall start with the study of compressed air, the uses of which range from producing the cooling breeze of the common electric fan to supplying the motive power for the high pressure pneumatic tools employed in industry. Low-pressure air such as is used in ventilation, air conditioning, combustion processes, drying, and the like is ordinarily required in great volume. These requirements are best met by fans or blowers of the centrifugal or rotary type. With these devices large volumes of air can be delivered at pressures from slightly above atmospheric to 25 lb per sq in. or even as high as 50 lb per sq in. gage. The solution of problems involving this type of air compression is largely based on empirical formulas provided in engineering and trade handbooks and need not be considered here.

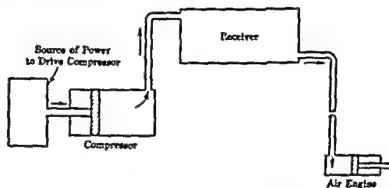


FIG. 6-1 Schematic Diagram of an Air Compression System

Air at gage pressures ranging from 25 lb per sq in. to 5000 lb per sq in. has a multitude of uses in industry in supplying motive power to such tools as drills, hammers, hoists, and presses. High pressure air is also

used as a means of transmitting power a considerable distance. In order to provide air at these high pressures the piston type of compressor must be used. It is also necessary to have a receiver, i.e., a storage tank, which receives the air from the compressor and acts as a source of steady supply for the air engine or motor. These three — the compressor, receiver, and engine — together with the connecting pipe lines, form the essential mechanical equipment of a compressed air cycle. It is with such a cycle, shown diagrammatically in Fig. 6-1, that we shall be particularly concerned.

Such a compressed air system is not a heat engine in the sense that the term has heretofore been used in discussing transformation of heat energy into mechanical work. Its primary purpose is not to transform a portion of the energy in a fuel into mechanical work but rather to transmit mechanical energy from one point to another through a series of thermodynamic processes. Air is an ideal medium for such a cycle because it is conveniently and abundantly available for use at all times and places. In this respect it has the same advantages that water has as a medium for vapor cycles. Since atmospheric air is almost completely a mixture of the so-called permanent gases, the various analyses in Chapter 4 pertaining to these gases may be applied here.

The Ideal Compressed Air Cycle

For various reasons any practical cycle must always deviate somewhat from the ideal. However, since an ideal cycle lends itself to clear thermodynamic analysis, it will be used as a basis for this discussion. Some attention will also be given to the various causes of departure from this cycle. Most modern compressors are of the double-acting type, in which air is compressed on both sides of the piston; but since no difference in fundamental analysis is involved, the compressor will be considered as single acting.

Figs. 6-2 and 6-3 show the processes of the cycle on the pV and TS planes respectively. In the discus-

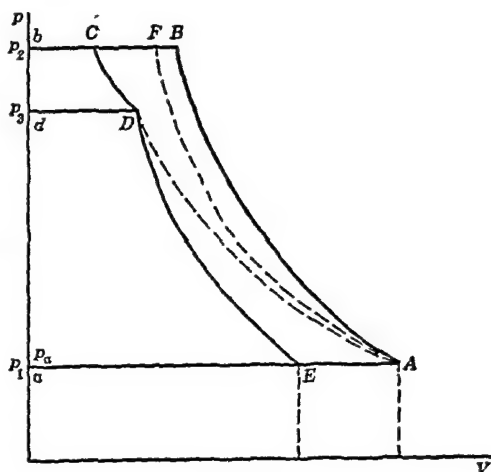


FIG. 6-2.

sion p_1 will denote initial pressure within the cylinder, and p_s will indicate the pressure of the immediately surrounding atmosphere. The volume at the initial state point A is the initial volume of air in the cylinder at pressure p_1 . For the ideal cycle without piston clearance this is also the volume of air drawn into the cylinder on the intake stroke. The compression, which is considered adiabatic in the

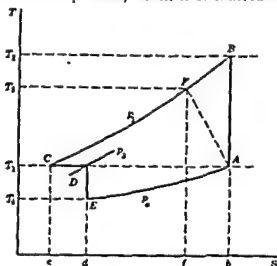


FIG. 6-3

ideal cycle, is represented by the curve AB and takes place during a part of the return stroke. The receiver pressure is denoted by p_2 , and when this pressure is reached (point B), the exhaust valves open. During the remainder of the stroke the volume of air represented by Bb , at pressure p_2 , is pushed bodily out of the cylinder and into the receiver without further change in volume. Because of the compression, the intrinsic energy of the air is greatly increased and its temperature T_2 is therefore greater than the initial atmospheric temperature. Since the outside of the receiver in which the compressed air is stored is in contact with the atmosphere, heat flows from it to the surroundings. The pressure in the receiver is maintained constantly at p_2 by the inflow of more air from the compressor so that the loss of heat results in a drop in the volume of the charge of air from Bb to Cb . This cooling process is represented on the TS plane by the constant-pressure line BC . It will be noted that ideally the air cools back to the atmospheric temperature T_1 in the receiver. Consequently, the increase in potential of the medium is that evidenced by the higher pressure p_2 .^{*} The loss of heat energy which occurs while the air is in the receiver is not desirable but is a necessary result of the practical operation of the cycle.

^{*} The student will find it profitable to refer again to the discussion of potential on page 92.

The net result of the cycle thus far has been to decrease the volume and increase the pressure of the air without permanent change of temperature and hence without change in intrinsic energy. This effect was brought about by work being done on the air. From this state, the air can expand to a lower pressure and hence to a temperature below atmospheric. Therefore it is capable of doing useful work at the expense of its intrinsic energy.

In order to reach the engine the air must pass through a pipe line in which there occurs a slight expansion and drop in pressure as work is done against flow friction. Since pipes for compressed-air systems are never insulated, the compressed air within the pipe is in temperature equilibrium with the surroundings and the expansion may be considered isothermal at atmospheric temperature. The expansion in the pipe line is represented by CD on both diagrams. The useful work of the cycle is done in the engine during the adiabatic expansion DE . At the end of this expansion the air exhausts to the atmosphere at temperature T_1 . The exhaust air absorbs heat from the body of atmospheric air with which it mingles and is eventually warmed to atmospheric conditions of pressure, volume, and temperature. This warming process is represented by EA on both diagrams. —

Work of the Compressor

The work done on the air by the compressor involves two distinct items. The first is the work of the adiabatic compression during the change AB , and the second is the work of moving the volume Bb of compressed air out of the cylinder against the receiver pressure. Heretofore emphasis has been placed on the fact that work of compression or expansion is readily obtained by integrating $\int p dV$. It should be kept in mind that $\int p dV$ gives the work of a *single* process. The work of a cycle, however, *must* be obtained by combining the separate values of $\int p dV$ for the work of the several processes, with proper algebraic signs. The work of the compressor is represented by the closed area $ABba$. This area is equal to the sum of the areas under AB and Bb taken to the V -axis, which represent work done *on* the medium, minus the area under aA , which represents work done *by* the incoming air on the piston. From the figures it follows that this amounts to finding the area between AB and the p -axis. It is shown in the calculus that such an area, in terms of the coordinates we have here, is given by $\int V dp$. Then the work of the compressor is

$$W_c = - \int_n^n V dp$$

The negative sign properly indicates work done on the medium.

In evaluating this integral, V is expressed in terms of p from the equation of the adiabatic curve AB , i.e.

$$pV^k = K \text{ (a const.)}$$

Then $V = Cp^{-1/k}$, where $C = K^{1/k}$

Substituting and integrating, we have

$$W_c = -C \int_p^2 p^{-1/k} dp = \frac{-Cp_2^{1-1/k} + Cp_1^{1-1/k}}{1 - \frac{1}{k}}$$

Since

$$\begin{aligned} C &= p_1 V_1^k = p_2 V_2^k \\ W_c &= \frac{p_1 V_1^{1-1/k} - p_2 V_2^{1-1/k}}{\frac{k-1}{k}} \\ &= \frac{k}{k-1} (p_1 V_1 - p_2 V_2) \end{aligned} \quad (1)$$

To avoid the necessity of determining V_2 , the equation may be reduced with the aid of $p_1 V_1^k = p_2 V_2^k$ to

$$W_c = \frac{k}{k-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{1/k} \right] \quad (2)$$

V_1 is the volume of air either per stroke or for any number of strokes, compressed from the initial state p_1, V_1, T_1 to the final pressure p_2 . To determine the horsepower developed in the cylinder, we may use the expression

$$\text{hp} = \frac{1}{33\,000} \frac{k}{k-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{1/k} \right] \quad (3)$$

in which case V_1 is the volume of air compressed per minute

By similar analysis the work done by the air engine is represented by the area $DEcd$ (Fig. 6-2) and is given by the equation

$$W_e = \frac{k}{k-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{1/k} \right] \quad (4)$$

in which p_1 and V_1 are the initial pressure and volume of air entering the engine and p_2 is the exhaust pressure

Another useful expression for the work of compression may be derived from Equation (1) and the equation $pV = MBT$

$$\begin{aligned} W_c &= \frac{k}{k-1} (MBT_1 - MBT_2) \\ &= \frac{k}{k-1} MB(T_1 - T_2) \end{aligned} \quad (5)$$

$$c_p = \frac{1}{J} B \frac{k}{k-1} \quad \text{so} \quad \frac{k}{k-1} B = Jc_p$$

Then

$$W_c = JM c_p (T_1 - T_2) \quad (6)$$

In this equation M represents pounds of air compressed and T_1 and T_2 are initial and final temperatures in the cylinder.

Because the cooling process in the receiver occurs at constant pressure the quantity of heat rejected is determined from the equation

$${}_BQ_C = Mc_p(T_1 - T_2) \quad (7)$$

Since, in the ideal case, the change BC is considered to be reversible, this quantity of heat is represented by the area $bBCc$ on the TS diagram in Fig. 6-3.

Source of Work Done by the Cycle

A comparison of Equations (6) and (7) reveals that the work of compression is *exactly equivalent* to the heat rejected in the receiver. This gives rise to speculation as to the source of the work done by the cycle. In order to clear this up and show that the cycle is no perpetual-motion affair, let us make a careful study of the energy influx and outgo for the cycle as a whole. Since an air compression cycle is a steady-flow process in which the same weight of air enters the compressor as exhausts from the engine in a given interval of time, the steady-flow Energy Equation is directly applicable. The equation between the compressor inlet and the receiver outlet is

$$\frac{Mu_A^2}{2g} + (E_A + p_A V_A) + (-J_B Q_C) = \frac{Mu_C^2}{2g} + (E_C + p_C V_C) + (-{}_A W_B)$$

Since the temperatures at the two state points A and C are identical, $E_A = E_C$ and $p_A V_A = p_C V_C$ and these terms cancel. When the rise in pressure is relatively high, the change in the kinetic-energy term is negligible; hence $\frac{Mu_A^2}{2g}$ and $\frac{Mu_C^2}{2g}$ may be omitted. The equation then reduces to

$$-J_B Q_C = -{}_A W_B \quad (8)$$

as shown in the preceding paragraph. If the equation is written between receiver outlet and compressor inlet for the flow through the pipe line, air engine, and atmosphere, we have

$$\frac{Mu_C^2}{2g} + (E_C + p_C V_C) + J_C Q_D + J_E Q_A = \frac{Mu_A^2}{2g} + (E_A + p_A V_A) + {}_D W_E + {}_C F_A \quad (9)$$

Because the temperatures at C and A are the same

$$E_C = E_A \quad \text{and} \quad p_C V_C = p_A V_A$$

${}_C Q_D$ represents heat which flows into the medium from the surrounding atmosphere during the passage through the pipe line. Actual isothermal flow through a pipe involves two separate energy trans-

formations. First, if the process is reversible, the work of expansion of the gas is manifested by the increase of kinetic energy that results from its increased velocity. Since the temperature is constant, intrinsic energy is constant, and so the equivalent of the work of expansion is supplied from the surroundings as heat. Therefore, in the absence of other effects, the heat added during reversible isothermal flow in a pipe is equivalent to the change in kinetic energy. The second energy transformation that takes place in actual pipe flow results from the fact that all such flow is frictional and hence irreversible. A certain amount of intrinsic energy is used to overcome the frictional resistance and is thereby transformed into heat. The latter remains in the system, where its presence operates to change the amount of heat added during the flow. Moreover, because of this transformation there has been an increase in unavailability which is manifested by a smaller velocity of flow and hence a smaller value of kinetic energy than would have been obtained had the flow been frictionless. Inasmuch as we are considering an ideal cycle, we shall consider the flow to be *reversible* (i.e., frictionless) and isothermal. Then $J_C Q_D$ is equivalent to the increase in kinetic energy of the air as it flows through the pipe. This energy is of course available at the intake to the air engine. Practically, the spent air is exhausted from the engine with the same velocity as that with which it enters. As the exhaust air mingles with the atmosphere, all of the stock of kinetic energy it possessed by reason of its velocity is dissipated to the atmosphere by turbulence and other frictional effects. Therefore $J_C Q_D = cF_A$. At both points C and A , the velocity of the air is negligible and the terms $\frac{Mfu_C^2}{2g}$ and $\frac{Mfu_A^2}{2g}$ may therefore be omitted. Equation (9) then reduces to

$$J_B Q_A = {}_B W'_X \quad (10)$$

which shows that the source of the work obtained from the cycle in the air engine is the heat absorbed from the atmosphere by the air as it warms from its state at exhaust to atmospheric conditions.

Although this statement answers the question concerning the source of the work done by the cycle, it is profitable to go one step further and establish the energy balance for the entire cycle. If Equations (8) and (10) are added, we have

$$-J_B Q_C + J_B Q_A = -{}_A W'_B + {}_B W'_X \quad (11)$$

${}_B W'_X$ is the work we obtain from the cycle, and ${}_A W'_B$ is the work supplied to the cycle. Consequently, from Equation (11), the net loss in energy for the whole cycle is equal to the difference between the heat rejected dur-

ing the change BC and that absorbed during the change EA . Since this is an ideal cycle in which all processes are reversible, the difference is shown on the TS diagram in Fig. 6-3 by the area $dEABCc$. We may say that this loss represents the cost in energy which must be paid for the convenience of using compressed-air machinery.

The foregoing discussion shows that the nature of the cycle is such that the price paid in energy is maximum and hence the efficiency is minimum. The optimum performance would be obtained if the area $dEABCc$ were reduced to a minimum. As may be seen from Fig. 6-3, this condition would be achieved if both compression and expansion were carried on *isothermally*. The work of compression would then be minimum and the work of expansion maximum. No practical method is available for changing the expansion in the engine to the isothermal condition. However, it is both possible and practicable to alter the nature of the compression so as to improve materially the efficiency of the cycle. We shall now give attention to the methods by which this improvement may be effected.

Water Jacketing

The energy stored in the air during the compression process is ordinarily not utilized but flows out of the system during the cooling process in the receiver. Hence any rise in temperature during compression indicates a useless expenditure of work. This waste of energy can be reduced by surrounding the cylinder with a jacket through which cooling water is circulated. The effect is to remove heat energy during the compression and thus cause the compression curve to tend toward the isothermal. Consequently, for an actual compressor, the typical equation of the compression curve in terms of p and V is $pV^n = \text{const.}$ The limits of n are 1.4 for adiabatic compression and 1 for isothermal compression. Water jacketing ordinarily causes the value of n to lie in the region of 1.3 to 1.35.

On the diagrams (Figs. 6-2 and 6-3) AB is the adiabatic path, AC the isothermal path, and AF the polytropic path which result from water jacketing. The saving in work is indicated by the area ABF on the pV and TS diagrams. The heat rejected to the water jacket is represented by the area $bAFf$ on the TS diagram. By substituting n for k , Equations (1) and (2) become

$$W_c = \frac{n}{n-1} (p_1 V_1 - p_2 V_2) \quad (12)$$

$$= \frac{n}{n-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} \right] \quad (13)$$

The heat given up to the cooling water may be determined by applying the equation

$$Q = Mc_p \Delta T$$

The specific heat for a polytropic change was shown on page 154 to be $C_p = C_v \left(\frac{k-n}{1-n} \right)$

$$C_p = C_v \left(\frac{k-n}{1-n} \right)$$

Substituting, we have

$$Q_{\text{water}} = Mc_p \left(\frac{k-n}{1-n} \right) (T_1 - T_2) \quad (14)$$

The heat rejected at constant pressure in the receiver is represented by the area $fFCc$ and

$${}_pQ_c = Mc_p (T_1 - T_2) \quad (15)$$

Adding these two equations to obtain the total heat rejected gives

$$\begin{aligned} {}_aQ_c &= M \left[c_p - c_v \left(\frac{k-n}{1-n} \right) \right] (T_1 - T_2) \\ &= M \left(\frac{c_p - nc_p - kc_v + nc_v}{1-n} \right) (T_1 - T_2) \\ &= M \frac{n}{n-1} (c_p - c_v) (T_1 - T_2) \\ &= \frac{n}{n-1} \frac{BM}{J} (T_1 - T_2) \end{aligned} \quad (16)$$

Since T_2 corresponds to pressure p_2 , $MBT_1 = p_1 V_1$ and $MBT_2 = p_2 V_2$, so that

$$J {}_aQ_c = \frac{n}{n-1} (p_1 V_1 - p_2 V_2)$$

Thus, as for the ideal cycle, the total heat rejected is equivalent to the work of compression

The following example will serve to illustrate the application of the equations derived

Example

4.7 cu ft of air are compressed and delivered per stroke from an initial pressure of 14.5 lb per sq in abs to a final pressure of 80 lb per sq in abs and final volume of 1.25 cu ft. Determine (a) the work of the compressor per stroke, (b) the work saved by water jacketing, (c) the heat rejected to the water jacket

* Bear in mind that since $\frac{k-n}{1-n}$ is negative for values of n between 1 and k , Q_{water} will be negative, as it should be to indicate heat flow from the system.

Solution

(a) It is first necessary to determine the value of the exponent n for this compression. Using the expression derived on page 39, we have

$$n = \frac{\log p_2 - \log p_1}{\log V_1 - \log V_2}$$

and substituting the given data, we find that n equals 1.29.

$$\begin{aligned} W_c &= \frac{n}{n-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} \right] \\ &= \frac{1.29}{0.29} \times 144 \times 14.5 \times 4.7 \left[1 - \left(\frac{80}{14.5} \right)^{\frac{0.29}{1.29}} \right] * \\ &= (-) 20,400 \text{ ft-lb per stroke} \end{aligned}$$

The negative sign properly indicates work done on the medium. The horsepower developed in the cylinder can be readily determined by considering the number of strokes per minute and applying the factor 1 hp = 33,000 ft-lb per min.

(b) To determine the saving in work, find the work required if the compression were adiabatic from

$$\begin{aligned} W_c &= \frac{k}{k-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right] \\ &= \frac{1.4}{0.4} \times 144 \times 14.5 \times 4.7 \left[1 - \left(\frac{80}{14.5} \right)^{\frac{0.4}{1.4}} \right] \\ &= (-) 21,600 \text{ ft-lb per stroke} \end{aligned}$$

The saving per stroke resulting from water jacketing is $21,600 - 20,400 = 1200$ ft-lb. This represents a saving in work of about $5\frac{1}{2}\%$.

(c) The heat rejected to the water jacket is

$$\begin{aligned} Q_J &= M c_v \frac{k-n}{1-n} (T_2 - T_1) \\ &= c_v \frac{k-n}{1-n} (M T_2 - M T_1) \end{aligned}$$

Since $pV = MBT$, $M T_1 = \frac{p_1 V_1}{B}$, $M T_2 = \frac{p_2 V_2}{B}$

$$\begin{aligned} Q_J &= 0.173 \left(\frac{1.4 - 1.29}{1 - 1.29} \right) \left[\frac{144}{53.3} (80 \times 1.25 - 14.5 \times 4.7) \right] \\ &= - 5.64 \text{ Btu per stroke} \end{aligned}$$

Multi-Stage Compression

It is impractical to carry out a compression ratio above 5 or 6 to 1 in a single cylinder because of the unwieldy size and weight of the cylinder required and the high final temperature involved. To avoid these difficulties compression is carried on in two or more stages, depending on the compression ratio to be attained. In the multi-stage compressor

* The log log slide rule affords a convenient means of evaluating the term $\left(\frac{80}{14.5} \right)^{\frac{0.29}{1.29}}$.

the air passes from the first cylinder through an intercooler before admission to the second cylinder, and so on. Water is circulated through coils in the intercooler to remove the heat of compression, the ideal effect sought is to lower the temperature to atmospheric in each intercooler.

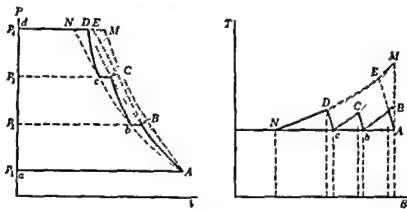


FIG. 6-4

This is seldom obtained, but a substantial reduction of work results from the cooling, as is indicated by the pV diagram (Fig. 6-4), which is representative of three-stage compression with complete intercooling.

AM represents the path of an adiabatic compression and AN the path of an isothermal compression between pressures p_1 and p_4 . AE represents a polytropic single stage compression. The path $ABbCcD$ shows the effect gained by multi staging with perfect intercooling, and the shaded area represents the work saved over that of an adiabatic single-stage compression. It will also be observed that there is a saving in work over that required for compression along the polytropic curve AE . Hence multi staging, in addition to avoiding excessively high temperatures and unwieldy cylinder size, also has the desirable effect of decreasing the total work of compression.

On the TS diagram the areas under AB , bC , and cD represent the heat rejected to the respective water jackets. Those under Bb and Cc represent the heat given up by the air in the receiver. The shaded area represents the heat equivalent of the work saved over adiabatic single stage compression. The work done in each cylinder may be computed from Equation (13) (page 207).

Volumetric Efficiency. Clearance

The capacity of a compressor is rated by the number of cubic feet of free air which it is capable of compressing per unit of time. Free air is defined as air at atmospheric temperature and pressure at the

location of the compressor. Thus far, our analysis has been concerned only with the compression of a given initial volume of air from its corresponding temperature and pressure to a new pressure. The present object is to determine the relationship between the volume of free air compressed per stroke of the piston and the volume swept through by the piston during that stroke. This relationship is affected by the practical necessity that a certain clearance be allowed between the piston and the cylinder head at the end of the stroke in order to avoid injury to the compressor if there is water or some other incompressible material in the cylinder.

The volume of air which remains in the clearance space at the end of the compression stroke acts as a cushion or spring and expands against the piston on the return stroke. In expanding, this air does the same work on the piston as was done on it by the compressor stroke. Hence there is no net effect on the work of compression from the action of the "cushion air." However, each time this volume of air expands back to the initial pressure, it occupies a certain volume of the cylinder which cannot be occupied by intake free air.

Another influence which must be considered in determining the volume of *free air* compressed per stroke is the slight reduction of the initial pressure within the cylinder below atmospheric pressure. This results from the creation of a slight partial vacuum by the piston on the intake stroke. It is this reduction in pressure which makes it possible for the atmospheric pressure to force free air through the intake valve.

Let us now refer to the pV diagram in Fig. 6-5 for the analysis of these effects. Atmospheric pressure is represented by p_a . Initial and final cylinder pressures are denoted by p_1 and p_2 respectively. V_c is the clearance volume and V_p is the volume swept through by the piston, often called the piston displacement volume.

As the piston reaches the end of the compression stroke and discharges, there is a volume of air V_c at pressure p_2 that remains in the cylinder. On the return intake stroke this volume of air expands along a path which may be considered to have the same equation as that of the compression, i.e.

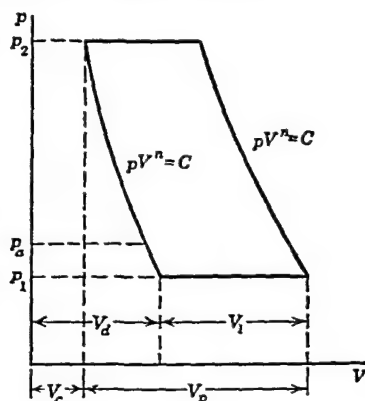


FIG. 6-5.

Therefore $p_1 l_a = \text{const}$
 $p_1 l_a = p_1 l_a'$

Then $l_a = l_a' \left(\frac{p_1}{p_a} \right)^{\frac{1}{\gamma}}$

is the volume occupied by this air at pressure p_1 . Since the volume of the cylinder is $V_c + l_a$, the remaining volume which may be occupied by air at pressure p_1 is $(V_c + l_a) - l_a$ which we shall call V_1 . If the free air is considered to enter the cylinder at constant temperature, which is substantially the case

$$p_1 V_1 = p_a V_a \quad \text{and} \quad V_a = \frac{p_1}{p_a} V_1$$

The ratio of V_a to V_c is called the volumetric efficiency

$$\eta_v = \frac{V_a}{V_c} = \frac{V_1 \frac{p_1}{p_a}}{V_c}$$

V_c may be expressed in terms of V_1 and of the clearance ratio $\frac{V_c}{V_1}$ in the following way

Since $V_1 = V_c + V_a - l_a$
 $V_1 = V_c + V_a - l_a \left(\frac{p_1}{p_a} \right)^{\frac{1}{\gamma}}$
 $= V_c \left[1 + \frac{V_a}{V_c} - \frac{1}{V_c} \left(\frac{p_1}{p_a} \right)^{\frac{1}{\gamma}} \right]$

Hence $V_c = \frac{V_1}{\left[1 + \frac{V_a}{V_c} - \frac{1}{V_c} \left(\frac{p_1}{p_a} \right)^{\frac{1}{\gamma}} \right]}$

Then $\eta_v = \frac{V_1 \frac{p_1}{p_a}}{\frac{V_1}{\left[1 + \frac{V_a}{V_c} - \frac{1}{V_c} \left(\frac{p_1}{p_a} \right)^{\frac{1}{\gamma}} \right]}}$
 $\eta_v = \frac{p_1}{p_a} \left[1 + \frac{V_a}{V_c} - \frac{1}{V_c} \left(\frac{p_1}{p_a} \right)^{\frac{1}{\gamma}} \right]$

Let the clearance ratio $\frac{V_c}{V_1}$ be given the symbol r , and

$$\eta_v = \frac{p_1}{p_a} \left[1 + r - r \left(\frac{p_1}{p_a} \right)^{\frac{1}{\gamma}} \right] \quad (17)$$

This equation expresses the volumetric efficiency in terms of atmospheric pressure, initial and final cylinder pressures, and the clearance ratio, all of which are easily observable quantities. The expression in

brackets is frequently called the clearance factor. The determination of n for any polytropic compression has been discussed on page 39. The following example illustrates the application of the above analysis.

Example

Determine the capacity of a single-acting compressor under the following conditions.

Atmospheric pressure, 14.7 lb per sq in. abs

Cylinder dimensions, 18-in. bore by 24-in. length

Clearance, 0.5 in.

Compressor speed, 100 rpm

$$p_1 = 14.5 \text{ lb per sq in. abs}$$

$$p_2 = 70 \text{ lb per sq in. gage}$$

$$= 84.7 \text{ lb per sq in. abs}$$

$$n = 1.33$$

Solution

$$\text{Cylinder volume} = \frac{\pi(1.5)^2}{4} \times 2 = 3.54 \text{ cu ft}$$

$$\text{Clearance volume } (V_c) = \frac{\pi(1.5)^2}{4} \times \frac{0.5}{12} = 0.074 \text{ cu ft}$$

$$V_p = 3.54 - 0.074 = 3.466 \text{ cu ft}$$

$$r = \frac{V_c}{V_p} = \frac{0.074}{3.466} = 0.0215$$

$$\eta_v = \frac{p_1}{p_a} \left[1 + r - r \left(\frac{p_2}{p_1} \right)^{\frac{1}{n}} \right]$$

$$\eta_v = \frac{14.5}{14.7} \left[1 + 0.0215 - 0.0215 \left(\frac{84.7}{14.5} \right)^{\frac{1}{1.33}} \right]$$

$$= 0.928$$

$$\text{Capacity} = V_a \times \text{strokes per min}$$

$$= V_p \times \eta_v \times 100$$

$$= 3.466 \times 0.928 \times 100 = 322 \text{ cu ft of free air per min}$$

The work of the compressor may now be computed by Equation (13).

$$W_c = \frac{n}{n-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} \right]$$

Since $p_1 V_1 = p_a V_a$ this equation may be written

$$\begin{aligned} W_c &= \frac{n}{n-1} p_a V_a \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} \right] \\ &= \frac{1.33}{0.33} 144 \times 14.7 \times 322 \left[1 - \left(\frac{84.7}{14.7} \right)^{\frac{0.33}{1.33}} \right] \\ &= 1,518,000 \text{ ft-lb per min} \end{aligned}$$

The corresponding horsepower is $\frac{1,518,000}{33,000} = 46 \text{ hp.}$

The last figure represents the horsepower required at the piston face for compressing and delivering the air and should not be confused with the power requirement for driving the compressor. The latter must of course include not only the power requirement for compression, but also sufficient power to make up for all energy losses resulting from friction of the mechanism.

At first it might be thought that consideration of volumetric efficiency should be given to each individual cylinder in multi stage compression. This is not the case. Once the air is in the first cylinder, the fact that the process is essentially one of flow requires that the same quantity must pass on to each succeeding cylinder. Inspection of Equation (17) discloses that η_v decreases as p_2 increases. Hence decreasing the final pressure in the first cylinder by multi staging has the effect of increasing volumetric efficiency.

The Air Engine

Let us now shift our attention from the process of compressing and delivering air to the receiver to the flow of the compressed air to the engine and its use therein. Ordinarily the engine is somewhat removed from the receiver so that the air must flow through a pipe line or hose before it is ready to do work by expanding in the engine. This flow causes some drop in pressure because of expansion and flow friction as discussed on page 203. The piston type air engine does not differ essentially from a steam engine in fact a steam engine may be driven by compressed air without change in its construction. Jack hammers and similar tools require special valve arrangements but these do not modify or change the thermodynamics of the air expansion. In the engine the expansion is usually so rapid that there is little or no heat interchange between the medium and the surroundings. The expansion may therefore be considered adiabatic.

The work of such an expansion represented by the area $dDEa$ (Fig 6-2), has already been shown to be

$$W_s = \frac{k}{k-1} (p_1 V_1 - p_2 V_2)$$

The expansion is accompanied by a temperature drop, as shown on the TS diagram (Fig 6-3). If the pressure range is great enough, this temperature drop may result in the freezing of any moisture contained in the air. If ice formation is excessive, it may create operating difficulties by causing the valves and other moving parts to stick. The trouble is not uncommon if encountered it can be avoided by reheating the air just before delivery. However, this is not the principal advantage

to be obtained from reheating, as will be shown in the following paragraphs.

Reheating

Reheating compressed air just before delivery to an air engine is often employed to increase the work of the engine. The effect of this process is schematically illustrated on the TS diagram in Fig. 6-6. The processes BJ , JE , and EF are the same as previously described in connection

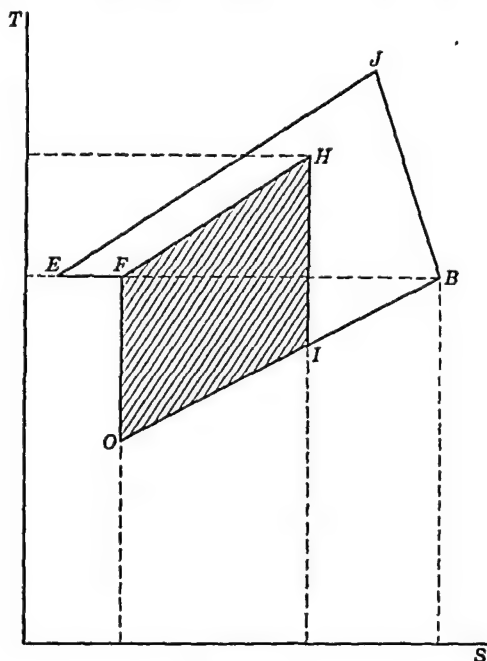


FIG. 6-6.

with Fig. 6-3. The air enters the reheater at the state shown by point F and absorbs heat at a constant pressure, as indicated by the path FH . As a result both temperature and volume increase. It follows that the increased energy of the air results in its being able to do more work per unit weight. The heat equivalent of the increase in work is represented by the shaded area in Fig. 6-6.

The process of reheating is practical and several types of reheaters are available. When the heat is supplied directly by the combustion of fuel, it has been found that the fuel requirement is about one-seventh of what would be necessary to develop the additional power required to increase the compression pressure enough to give the same engine

output. When it is convenient to use heat which would otherwise be wasted, such as the heat in exhaust steam or flue gases, a more pronounced economy naturally results.

Overall Efficiency of the Compressed Air Cycle

The overall efficiency of the compressed air plant necessarily depends on the ratio of the work done by the engine to the total energy supplied to the cycle. Before leaving this subject it is worth while to note the important influences which govern this ratio. There are a number of losses which may occur from the moment a certain quantity of air enters the compressor until it leaves the engine. They may be summarized as follows:

- 1 Entrance of air to the compressor at a temperature above atmospheric. This results in a lower weight of air being compressed per stroke. Further the resulting higher temperatures cause an increase in the power required to compress a given weight of air. The air supply should be taken from the coolest available spot.
- 2 Mechanical friction in the compressor.
- 3 Mechanical imperfection in the compressor cylinders, i.e., insufficient valve openings and leaky valves and piston rings.
- 4 Inefficient jacket cooling with resultant high temperature and increased work of compression.
- 5 Flow friction in the pipe line, resulting in loss of both energy and pressure.
- 6 Loss of air in the pipe line due to leaks.
- 7 Mechanical friction in the engine.
- 8 Incomplete expansion in the engine. Complete expansion to atmospheric pressure is not practical for the following reasons:
 - a The cylinder must be large.
 - b The air must exhaust at a pressure above atmospheric to overcome friction and the back pressure of the atmosphere.
 - c Unless reheating is employed the temperature may drop so low as to cause freezing of the moisture around the exhaust valves.

PROBLEMS

- 1 Show the complete ideal compressed air cycle on $p\bar{v}$ and TS diagrams. Discuss the processes occurring around the cycle and indicate the device in which each one occurs. State where work is done on or by the cycle and where and how heat flows.
- 2 Illustrate with $p\bar{v}$ and TS diagrams the effect of water jacketing an air compressor cylinder. Discuss the advantages which result from water jacketing.

3. What horsepower is needed to compress and deliver 1500 cu ft of free air per min to a receiver in which the pressure is constant at 44.1 lb per sq in. gage? Initial pressure within the cylinder is 14.3 lb per sq in. abs. Atmospheric pressure is 14.7 lb per sq in. abs. $n = 1.3$. Clearance 10%.
4. Define free air, clearance, and volumetric efficiency, and state their relation to air compression analysis.
5. Illustrate the effect of multi-stage air compression by pV and TS diagrams. Why is volumetric efficiency concerned only with the first stage in multi-stage compression?
6. Air initially at 15 lb per sq in. abs and temperature of 70° F is compressed according to the path equation

$$pV^{1.33} = \text{const}$$

to a pressure of 75 lb per sq in. abs and is then cooled at this pressure to 70° F. Find (a) the total heat rejected in the receiver per pound of air

$$c_p = 0.24 \quad c_v = 0.17$$

(b) the heat removed in the water jacket.

7. Show the effect of clearance in air compressors on a pV diagram and locate the coordinates which give the volume of intake air, the clearance volume, and the piston displacement volume. How is the volume of intake air related to the volume of *free* air, and what is the volumetric efficiency?
8. Why is less work required in compressing air to a given pressure isothermally than is required when the process is carried out adiabatically?
9. What is the meaning of the sentence, "Don't make a Diesel engine out of your air compressor," which has appeared in an advertisement for compressors?
10. What is the result of heating compressed air just before its admission to the air engine? If this heating is done by the admission of steam to the air line, what precautions must be taken?
11. Why is it, since in a compressed-air system all of the work of compression is given up as heat in the intercooler or receiver or both, that work can still be done by the air expanding back to atmospheric pressure?
12. Find the theoretical horsepower developed by 3 cu ft of air per min that has a pressure of 200 lb per sq in. abs if it is admitted and expanded in an air engine with one-fourth cutoff. The value of n is 1.2. (Neglect clearance.)
13. What is the temperature in the exhaust pipe of an engine, if air is supplied at 100 lb per sq in. abs and 70° F and expands adiabatically to atmospheric pressure? (12 lb per sq in. at location.)
14. What volume must be provided in an air receiver to hold 20 lb of air if the pressure is 250 lb per sq in. gage and the temperature 100° F? If the temperature then drops at const p to 70° F, what will be the volume? What additional weight of air at 250 lb per sq in. gage and 70° F must be supplied to maintain the constant pressure?

Internal Combustion Engines; the Otto and Diesel Cycles

Early Developments

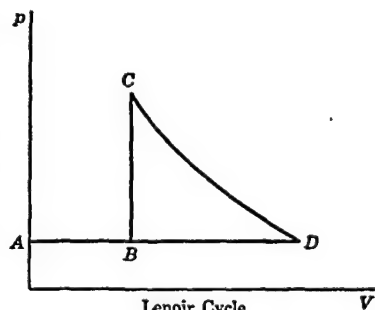
In the preceding discussion of the compressed air cycle it was pointed out that reheating offers a means of increasing the energy content of the air, and thus provides for an increased output of work by the engine. This idea easily leads to the thought that a cycle with air as the medium might be arranged to transform heat energy into work. The conclusion is not new. In the early part of the nineteenth century several investigators proposed such a cycle.

Robert Stirling, an Englishman, built a hot air engine designed to utilize the expansive power of furnace-heated air. John Ericsson, a later inventor and the builder of the *Monitor*, designed and built hot air engines which were installed in a 2200-ton ship. These engines had four single-acting cylinders 14 ft in diameter, and operated with a piston stroke of 6 ft. With an engine speed of 9 rpm, the plant developed 300 hp. Air has two physical properties which greatly affected the design and operation of Ericsson's engine. Its relatively low specific heat required an enormous cylinder size in comparison with the horsepower developed, and its relatively low conductivity caused the metal separating the furnace and the medium to become too hot to withstand continued use. For these reasons the hot air engine was found impractical and its use has been abandoned. Historically these attempts are of interest because they had a place in the development of the science of engineering thermodynamics and show the trend of thought at that time.

The development of the steam engine produced a practical heat motor, but thoughtful investigators sought a more efficient means of transforming heat into work. Taking cognizance of the relatively low temperatures associated with working steam pressures and the loss of availability of energy occasioned by the flow of heat from high furnace temperature to low steam temperature, these investigators tried to devise a way to utilize the heat at a temperature nearer to that of combustion. After Stirling's and Ericsson's unsuccessful attempts with

external combustion cycles, in which the medium was heated by a separate furnace, this approach to the problem was abandoned. Attention was then given to the possibility of carrying on the combustion *within the working cylinder itself*. This idea proved practical and the resulting cycle, appropriately called an *internal combustion cycle*, is widely used today. In an internal combustion engine the hot gaseous products of combustion constitute the medium.

The first internal combustion engine to attain any degree of commercial success was the Lenoir engine patented in France in 1860. It operated on a two-stroke cycle as follows (Fig. 7-1): The gaseous mixture of fuel and air was admitted to the cylinder at atmospheric pressure for about half the downstroke (AB). As the inlet valves closed, the charge was ignited. There resulted a quick rise in pressure (BC), followed by expansion and power delivery during the remainder of the stroke (CD). On the return stroke (DA), the products of combustion were swept out of the cylinder.



Lenoir Cycle

FIG. 7-1.

The engine was also made double-acting by carrying out the cycle alternately on each side of the piston. The Lenoir cycle was not very efficient and soon went into disuse when other inventors perceived the possibility of increasing the temperature of combustion, and hence improving efficiency, by *compressing the air and fuel mixture within the cylinder before ignition*.

In a patent obtained in Paris in 1862, Beau de Rochas stated the principles and the requisite cycle of operation for an internal combustion engine in which compression of the fuel mixture was an essential feature. The Otto engine, brought out in 1876, operated on the same compression cycle that Beau de Rochas had proposed. The Otto engine is said to have been invented independently of knowledge of Beau de Rochas' work. In any event, the cycle has acquired the name "Otto cycle" and is the one used in the modern gasoline engine.

Contemporaneous with the work of Beau de Rochas and Otto, a different idea for an internal combustion cycle was presented. It proposed that the air required for combustion should be *compressed before mixture with the fuel*. This idea was used in an engine patented in 1872 by an American, George B. Brayton. In the Brayton engine, air compressed by a separate unit, together with gasoline or kerosene

vapor, was admitted to the cylinder at the beginning of the power stroke. The mixture was immediately ignited and the admission of compressed air and fuel continued for the first part of the power stroke. The effect produced was practically a constant-pressure burning and expansion until fuel and air were cut off, followed by expansion with declining pressure to the end of the stroke. This engine was not a commercial success because of the complexity of its equipment and the danger of external explosion. In 1893 Rudolf Diesel invented the Diesel engine, which successfully employs the principles of the Brayton engine by *compressing air alone within the cylinder*. The constant-pressure slow-burning effect is obtained approximately by injecting liquid fuel during the initial part of the power stroke.

The Otto Cycle

Since modern internal combustion engine development is focused on the Otto and Diesel cycles, we shall consider the essential features of each in some detail. The gasoline engine so widely used in the automobile is a common example of the application of the Otto cycle. This cycle is also employed extensively in marine and stationary engines,

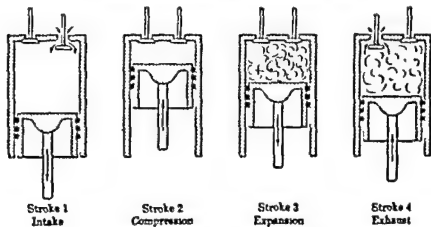


FIG. 7-2 Piston Movement for Four Stroke Internal Combustion Engine

particularly for those of relatively small size. In this type of engine gasoline vapor or combustible gas, mixed with air in a carburetor, enters the cylinder through the intake valve during the downstroke of the piston (stroke 1) (see Fig. 7-2). At the bottom of this stroke, the intake valve closes and the mixture is compressed on the return stroke (stroke 2). At the end of the compression stroke the mixture is ignited by an electric spark and combustion occurs with explosive effect and hence at nearly constant volume. Expansion of the products of combustion forces the

piston down (stroke 3) and work is delivered to the crankshaft. The following upstroke (stroke 4) of the piston clears the cylinder of the products of combustion and the cycle begins anew. Because four strokes are required for its completion, this cycle is commonly referred to as a four-stroke cycle and the engine which operates on it is called a four-stroke-cycle engine, or sometimes simply a four-cycle engine.

The two-stroke-cycle engine, which is a modification of the above type, is designed to permit entrance of the fuel mixture via the crankcase. Sufficient pressure is developed in the crankcase so that, with suitable port arrangement, the fuel enters the cylinder and displaces the products of combustion immediately after the expansion or working stroke. The ports then close and the mixture is compressed as in the four-stroke cycle. The cycle therefore dispenses with the intake and exhaust strokes of the four-stroke cycle and completes its operation in only two strokes of the piston. In some modern two-stroke-cycle engines, crankcase compression has been eliminated by using separate scavenging blowers.

In a multiple-cylinder engine the operation of each cylinder is a cycle unto itself. At a given instant, each cycle is at a different stage of progress. By proper spacing of the working strokes of the several cylinders, an almost uniform turning effort is supplied to the crankshaft.

The distinctive features of the engine that employs the Otto cycle are: (1) the mixing of air and fuel outside the cylinder, (2) the compression of this mixture within the cylinder before ignition, and (3) combustion of the mixture at nearly constant volume. The characteristics of the fuels used in this cycle impose a limitation on the ratio of compression that may be used, first, because spontaneous pre-ignition may occur if the temperature resulting from compression is sufficiently high, and second, because most fuels suitable for use in the Otto cycle detonate if ignited when under excessively high pressure. The term "ratio of compression" used in the preceding sentence signifies the quotient of the volume of the medium at the beginning of the compression stroke and the clearance volume. Because of the great thermodynamic advantage to be gained from a high compression ratio, a great deal of research has been and is now being carried on to develop fuels suitable for use in engines designed to operate with such a ratio. The present ratio of 6 or 7 to 1 used in automobile engines will doubtless give way to higher ratios as fuel development progresses.

The Diesel Cycle

The ordinary Diesel engine may also operate on a four-stroke cycle but has the *distinctive feature that air alone is compressed in the cylinder.* Because of this it is not subject to the limitation of the compression ratio

imposed on the Otto cycle. Higher compression ratios require engines of heavier construction. Consequently the Diesel weight per unit horsepower is high in comparison with Otto engines. Up to the present time the Diesel engine has been used principally for stationary power plants, marine service, and heavy-duty transportation units. However, the trend seems to indicate a more general use of these engines in automobiles and airplanes.

The cycle of operation of the four-stroke-cycle Diesel engine is as follows (see Fig. 7-2). Air enters the cylinder on a downstroke of the piston and is compressed on the return stroke. Compression ratios of 12 to 1 and over are common, and frequently the intake air is supplied to the engine at a pressure well above atmospheric. Near the end of the compression stroke liquid fuel is injected into the cylinder through a spray valve. As a result of the high compression, the temperature of the air is sufficiently high to cause spontaneous combustion of the atomized fuel immediately upon its entrance into the cylinder. Thus the standard type Diesel engine requires no ignition system. The rate and duration of fuel injection are controlled to obtain efficient combustion and there results a practically constant pressure expansion during the combustion process. After the completion of fuel injection and combustion, expansion of the products of combustion, with declining pressure, continues for the remainder of the working stroke. During the following upstroke of the piston the products of combustion are swept from the cylinder, thus completing the cycle.

The two-stroke cycle is also applied extensively in Diesel engine design.* In fact, large installations are frequently built both two-cycle and double-acting in order to avoid excessive size and weight.

Methods of Computing Efficiencies of Internal Combustion Engines

Several different approaches may be made to the study of the performance and efficiency of internal combustion engines of both the Otto and Diesel types. The value and importance of each method depend largely upon the extent and purpose of the information desired. For example, one item in which the manufacturer and operating engineer are vitally interested is the actual power output under varying operating conditions. They are also interested in the fuel required per unit of power developed. While the designing engineer may also be striving for maximum power output together with good fuel economy, his study must include a detailed analysis of the underlying thermodynamic principles involved.

* Discussion of two-cycle engines and other modifications of the application of the Otto and Diesel cycles may be found in any standard text on internal combustion engines. See J. A. Poulos, *Internal Combustion Engines*, Wiley.

Indicated Power and Brake Power

The indicator diagram provides one direct means of obtaining information concerning the operating performance of an engine. Typical indicator diagrams from Otto and Diesel engines are shown in Figs. 7-3 and 7-4 respectively. These diagrams are obtained by use of the so-called *engine indicator*. This device is attached to the engine cylinder

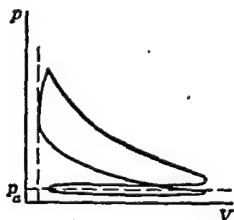


FIG. 7-3. Typical Indicator Diagram of Four-Stroke Otto Cycle. (Pump loop exaggerated.)

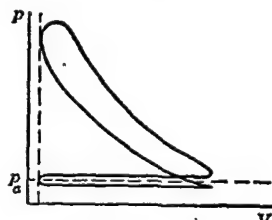


FIG. 7-4. Typical Indicator Diagram of Four-Stroke Diesel Cycle. (Pump loop exaggerated.)

and by its operation traces on the indicator card a graphic record of the pressure-volume changes around the cycle. A calibrated scale relates the actual pressure and volume within the cylinder to all points on the diagram * (see also page 49).

Figs. 7-3 and 7-4 show that the engine indicator traces a closed cycle on the pV diagram. It should be recalled that the area of any closed cyclical diagram is a representation of the net work of the cycle. Practical use of the diagram involves the computation of the *mean effective pressure*. This pressure is simply the mean ordinate of the indicator diagram, or the constant pressure which, if applied unopposed to the piston during the power stroke, would produce an amount of work equal to the net work of the cycle. The closed area of the diagram may be measured with a planimeter; if this area is divided by the length of the diagram, the quotient times the pressure scale equals the *mean effective pressure*.

The work evidenced by the diagram is the work accomplished by the expanding medium *at the piston face*; it is called the *indicated work of the cycle*. We may compute indicated work with the formula

$$\text{Indicated work of cycle} = p_m AL$$

Then the indicated horsepower (Ihp) for the cylinder = $\frac{p_m LAN}{33,000}$
in which

* The A.S.M.E. Test Code limits the use of indicators to engines operating at speeds under 400 rpm.

p_m = mean effective pressure in pounds per square inch absolute

L = length of stroke in feet

A = area of the piston face in square inches

N = number of cycles per minute

For a four-stroke-cycle engine $N = \frac{\text{rev per min}}{2}$

For a two-stroke-cycle engine $N = \text{rev per min}$

For a double-acting two-stroke-cycle engine $N = 2 \times (\text{rev per min})$

For a multi-cylinder engine we must of course make a summation of the power developed in all the cylinders to obtain the indicated horsepower of the engine. The ratio of the heat equivalent of the indicated horsepower per hour to the heating value of the fuel consumed per hour is the indicated thermal efficiency of the engine.

Actual power delivered to the engine shaft, called *brake power*, may be determined by tests with a brake dynamometer, sometimes called a "pronybrake." Comparison of the net work, thus determined, with the heating value of the fuel consumed for the same unit of time yields the *overall* thermal efficiency, a more reliable index of the efficiency of high-speed engines. The difference between indicated horsepower and brake horsepower is accounted for by the energy dissipated in overcoming mechanical friction of the moving parts. Hence, the ratio between the two gives the mechanical efficiency of the engine.

Example

Indicator cards taken on each of the six cylinders of a four-cycle Diesel engine disclose the mean effective pressures to be 92, 100, 92, 102, 98, 95 lb per sq in respectively. The diameter of the cylinders is 13 in and the piston stroke is 13.5 in. The fuel consumption is 183.4 lb of oil (heating value 19,150 Btu per lb) per hour for an average engine speed of 400 rpm. At this speed, the brake horsepower is measured as 415 hp. Determine (a) the indicated horsepower, (b) the indicated thermal efficiency, (c) the mechanical efficiency, (d) the overall thermal efficiency of the engine.

Solution

$$(a) \text{ Indicated horsepower} = \frac{p_m LAN}{33,000}$$

We may take the average MEP as p_m .

Then

$$p_m = 96.5 \text{ lb per sq in.}$$

$$L = 13\frac{1}{2} \text{ in} = \frac{9}{8} \text{ ft}$$

$$A = \frac{\pi \times (13)^2}{4} \text{ sq in}$$

$$N = \frac{400}{2} = 200 \text{ cycles per cyl per min}$$

$$\text{Number of cylinders} = 6$$

$$\begin{aligned} \text{I hp} &= \frac{6 \times 144 \times 96.5 \times \frac{9}{8} \times \pi \times (13)^2 \times 200}{33,000 \times 8 \times 4 \times (12)^3} \\ &= 524 \text{ hp} \end{aligned}$$

- (b) Indicated thermal efficiency equals

$$\frac{\text{Indicated output}}{\text{Fuel input}} = \frac{524 \times 33,000 \times 60}{183.4 \times 19,150 \times 778} = 0.38 \text{ or } 38\%$$

- (c) Mechanical efficiency equals

$$\frac{\text{Brake hp}}{\text{I hp}} \times 100 = \frac{415}{524} \times 100 = 79.2\%$$

- (d) Overall thermal efficiency equals

$$\frac{\text{Brake output}}{\text{Fuel input}}$$

but is also easily determined as the product of indicated thermal efficiency and mechanical efficiency, thus

$$0.38 \times 0.792 = 0.301 \text{ or } 30.1\%$$

The above analysis has a very practical use. It affords a means of comparing the performance of a particular engine under varying operating conditions, of comparing different engines, and of establishing a basis for rating engines. On the other hand, it affords little help in ascertaining the relative influence of the several processes whose combined effect produces the observed result.

The Ideal Four-Stroke Otto Cycle

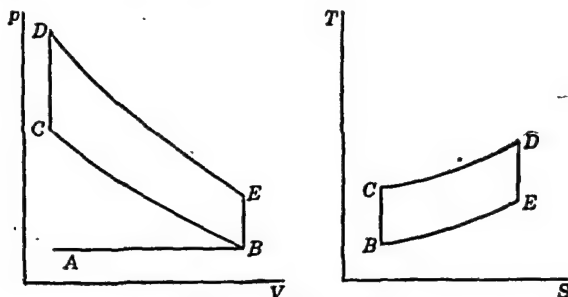


FIG. 7-5. Otto Cycle.

Stroke	pV diagram	TS diagram
1	A $\xrightarrow{\hspace{2cm}}$ B Intake of carburetor mixture. Constant-pressure flow work done by medium	Intake, point B
2	C $\xleftarrow{\hspace{2cm}}$ B Adiabatic compression. Work done on medium. At C, ignition by spark. CD, constant-volume combustion	BC, adiabatic compression. Point C, ignition. CD, constant- volume combustion with addition of heat to medium

Stroke	pV diagram	TS diagram
3	$D \xrightarrow{\hspace{2cm}} E$ Adiabatic expansion Work done by medium (power stroke) EB , constant volume exhaust	DF adiabatic expansion. EB constant volume exhaust with rejection of heat by cycle
4	$A \xleftarrow{\hspace{2cm}} B$ Scavenging Products of com- bustion swept from cylinder Constant pressure flow work done on medium	Scavenging point B

Air Standard Analysis

A simple, though artificial, efficiency analysis which has been employed extensively as a basis for studying internal combustion engine cycles is the so-called *air standard* method. Although air-standard efficiency is at best a mere approximation, it does indicate the effects of compression and expansion and may serve as a basis for the comparison of different engines. So that the student may obtain an appreciation of the significance of air standard analysis, we shall use it to derive expressions for the efficiency of both Otto and Diesel cycles.

Air Standard Efficiency, Otto Cycle

Fig. 7-5 shows the ideal Otto cycle on the pV and TS diagrams together with descriptions of the processes of the cycle as related to the piston strokes. A comparison of this pV diagram with the indicator card for an actual Otto cycle (Fig. 7-3) immediately reveals that certain assumptions are made for the ideal cycle. For air-standard analysis these assumptions are as follows:

- 1 The pressure during the intake stroke AB and the exhaust stroke BA is the pressure of the atmosphere.
- 2 The processes BC and DE are adiabatic.
- 3 The medium throughout the entire cycle is air.
- 4 The specific heat of air is constant during any of the changes of the cycle, and $n = k = 1.4$ in $pV^n = \text{const.}$
- 5 A quantity of heat equivalent to the energy released by combustion of fuel in the actual process is added to the air during the constant volume change CD .
- 6 The cycle is closed and a quantity of energy leaves the system during process EB equal to the heat lost in a constant volume cooling of air from T_E to T_B .

With these assumptions, the thermal efficiency of the cycle is

$$\eta = \frac{\text{output}}{\text{input}} = \frac{Q_1 - Q_2}{Q_1}$$

$$Q_1 = Mc_v(T_D - T_C)$$

$$Q_2 = Mc_v(T_E - T_B)$$

Therefore

$$\eta = \frac{Mc_v(T_D - T_C) - Mc_v(T_E - T_B)}{Mc_v(T_D - T_C)}$$

$$= 1 - \frac{(T_E - T_B)}{(T_D - T_C)} \quad (1)$$

By taking cognizance of the assumptions that changes BC and DE are adiabatic, that the clearance volume $V_C = V_D$ and that $V_E = V_B$, we may set up the following relationships.

$$\frac{T_B}{T_C} = \left(\frac{V_C}{V_B}\right)^{k-1}$$

$$T_B = \left(\frac{V_C}{V_B}\right)^{k-1} T_C$$

$$\frac{T_E}{T_D} = \left(\frac{V_D}{V_E}\right)^{k-1} = \left(\frac{V_C}{V_B}\right)^{k-1}$$

$$T_E = \left(\frac{V_C}{V_B}\right)^{k-1} T_D$$

By substitution in Equation (1)

$$\eta = 1 - \frac{\left(\frac{V_C}{V_B}\right)^{k-1} (T_D - T_C)}{(T_D - T_C)} = 1 - \left(\frac{V_C}{V_B}\right)^{k-1}$$

V_C is the clearance volume and $\frac{V_B}{V_C}$ is the compression ratio (r).

Then

$$\eta = 1 - \frac{1}{(r)^{1.4-1}} = 1 - \frac{1}{(r)^{0.4}}$$

The following example exemplifies the application of the above analysis.

Example

An Otto cycle engine uses 0.65 lb of oil per hp-hr (heating value of oil, 19,000 Btu per lb). The clearance is 22% of the piston displacement. $k = 1.4$. (a) Determine the compression ratio. (b) Compute the actual thermal efficiency and its ratio to the air-standard efficiency. (c) What is the ratio of the air-standard efficiency of this engine to that of an engine having a compression ratio of 4.6?

Solution

$$\begin{aligned}
 (a) \quad V'_C &= 0.22(V_B - V_C) \\
 V'_C &= 0.22 V_B - 0.22 V_C \\
 0.22 V_B &= 1.22 V_C \\
 r = \frac{V_B}{V_C} &= \frac{1.22}{0.22} = 5.5
 \end{aligned}$$

$$\begin{aligned}
 (b) \quad \text{Air-standard efficiency} &= 1 - \frac{1}{(r)^{k-1}} = 1 - \frac{1}{(5.5)^{0.4}} \\
 \eta_1 &= 1 - 0.506 \\
 \eta_1 &= 0.494 = 49.4\%
 \end{aligned}$$

$$\begin{aligned}
 \text{Actual thermal efficiency} &= \frac{\text{output}}{\text{input}} \\
 \text{Output 1 hp-hr} &= 2545 \text{ Btu} \\
 \text{Input per hp-hr} &= 0.65 \times 19,000 = 12,350 \text{ Btu} \\
 \eta_2 &= \frac{2545}{12,350} = 20.6\% \\
 \text{Ratio of efficiencies } \frac{\eta_2}{\eta_1} &= \frac{20.6}{49.4} = 0.417
 \end{aligned}$$

(c) For an engine with a compression ratio of 4.6

$$\begin{aligned}
 \eta_2 &= 1 - \frac{1}{(4.6)^{0.4}} = 1 - 0.543 = 0.457 \\
 \frac{\eta_2}{\eta_1} &= \frac{49.4}{45.7} = 1.08
 \end{aligned}$$

The work of an ideal Otto cycle, air standard, may be determined from the following considerations

- 1 The net value of the work of processes AB and BA is zero
- 2 ${}_B W'_C = \frac{p_C V'_C - p_B V'_B}{1-k}$, work of an adiabatic compression done on the medium
- 3 ${}_C W'_D = 0$, constant volume change
- 4 ${}_D W'_B = \frac{p_B V'_B - p_D V'_D}{1-k}$, work of an adiabatic expansion done by the cycle

Therefore, $W'_{net} = {}_D W'_B - {}_B W'_C$

The value to the student in making a computation of this sort is great. Through it he gains an appreciation of the order of magnitude of pressure and temperature at all points of the cycle. Actually, however, the assumption upon which air standard efficiency is based is so arbitrary that the value of this sort of study is decidedly restricted for the solution of problems either of design or of operation. Consequently the following example is to be studied for the information it gives concerning the

method of cyclical analysis rather than as an illustration of actual engine design.

Example

The cylinders of an Otto cycle engine are 8 in. in diameter. The stroke is 12 in. and the compression ratio is 6 to 1. At the beginning of compression the pressure is 14.7 lb per sq in. abs and the temperature is 150° F. The final temperature of the combustion phase is 3900° F. Compute the net work per cylinder for one cycle.

Solution

A diagram (Fig. 7-6) will be helpful in carrying out the solution.

V_p is the volume swept through by the piston

$$V_p = \pi \times \left(\frac{8}{2}\right)^2 \times 1 = \frac{\pi}{9} \text{ cu ft}$$

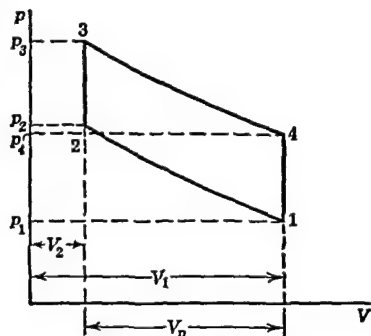


FIG. 7-6.

Since the compression ratio is 6 to 1

$$V_1 = \frac{6}{5} \times V_p = \frac{6}{5} \times \frac{\pi}{9} = \frac{6\pi}{45} = 0.418 \text{ cu ft}$$

$$p_1 = 14.7 \text{ lb per sq in. abs}$$

From the air-standard assumption, $k = 1.4$

$$p_1 V_1^k = p_2 V_2^k$$

$$p_2 = p_1 \left(\frac{V_1}{V_2}\right)^k = 14.7(6)^{1.4} = 180.7 \text{ lb per sq in. abs}$$

Work of compression equals area under curve 1-2

$${}_1W_2 = \frac{p_2 V_2 - p_1 V_1}{1 - k} = \frac{V_1 \left(p_2 \frac{V_2}{V_1} - p_1 \right)}{1 - k} = \frac{V_1 \left(p_2 \times \frac{1}{6} - p_1 \right)}{1 - k}$$

$${}_1W_2 = \frac{144 \times 0.418 \left(\frac{180.7}{6} - 14.7 \right)}{1 - 1.4}$$

$${}_1W_2 = \frac{144 \times 0.418 \times 15.42}{-0.4} = (-) 2320 \text{ ft-lb}$$

$$T_1 = 150 + 460 = 610^\circ \text{ R}$$

$$T_2 = T_1 \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = 610 \left(\frac{180.7}{14.7}\right)^{\frac{0.4}{1.4}} = 1250^\circ \text{ R}$$

$$T_3 = 3900 + 460 = 4360^\circ \text{ R}$$

Since $V_2 = V_3$

$$\frac{p_2}{T_2} = \frac{p_3}{T_3}; p_3 = \frac{180.7}{1250} \times 4360 = 630 \text{ lb per sq in. abs}$$

The ratio between V_3 and V_4 is the same as that between V_2 and V_1 , i.e.

$$\frac{V_3}{V_4} = \frac{1}{6}$$

Also $p_1 V_1^k = p_4 V_4^k$

So $p_4 = p_1 \left(\frac{V_1}{V_4} \right)^k = 630 \left(\frac{1}{6} \right)^{1.4} = 51 \text{ lb per sq in. abs}$

$$\begin{aligned} \text{Work of expansion} &= \frac{p_4 V_4 - p_3 V_3}{1 - k} = \frac{V_4 \left(p_4 - p_3 \frac{V_3}{V_4} \right)}{1 - k} = \frac{V_4 \left(p_4 - \frac{p_3}{6} \right)}{-0.4} \\ &= \frac{144 \times 0.418 (51 - 105.0)}{-0.4} \\ &= \frac{144 \times 0.418 (-54)}{-0.4} = 8140 \text{ ft lb} \end{aligned}$$

The enclosed area on the diagram represents the *net* work of the cycle, and so

$$W_{\text{cycle}} = 8140 - 2320 = 5820 \text{ ft lb}$$

The Ideal Four Stroke Diesel Cycle

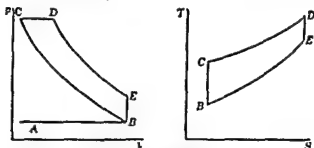



FIG. 7-7 Diesel Cycle

Stroke	pV diagram	TS diagram
1	$A \longrightarrow B$ Intake of air at constant pressure Work done <i>by</i> medium	Intake of air, point B
2	$C \longleftarrow B$ Adiabatic compression of air Work done <i>on</i> medium	BC , adiabatic compression
3	$C \longrightarrow D$ Fuel injection with combustion and <i>constant pressure</i> expansion begins at C and continues during process CD Work done <i>by</i> medium	CD , fuel injection and constant-pressure combustion Heat <i>added</i> to medium
	$D \longrightarrow E$ Adiabatic expansion of products of combustion Work done <i>by</i> medium	DE , adiabatic expansion

Stroke	pV diagram	TS diagram
	EB , exhaust at constant volume	EB , exhaust. Heat rejected by the cycle
4	 Scavenging of products of combustion at constant pressure. Work done on medium	Scavenging, point B

Air-Standard Efficiency, Diesel Cycle

In analyzing the Diesel cycle on the air-standard basis the same assumptions are made as were listed on page 226 for the Otto cycle except that, for the Diesel cycle, process CD is assumed to occur at *constant pressure*.

Since for any cycle $\eta = \frac{Q_1 - Q_2}{Q_1}$

and for the cycle under consideration

$$\begin{aligned}
 Q_1 &= M c_p (T_D - T_C) \\
 \text{and} \quad Q_2 &= M c_v (T_E - T_B) \\
 \eta &= \frac{M c_p (T_D - T_C) - M c_v (T_E - T_B)}{M c_p (T_D - T_C)} \\
 \eta &= 1 - \frac{c_v}{c_p} \left(\frac{T_E - T_B}{T_D - T_C} \right) = 1 - \frac{1}{k} \left(\frac{T_E - T_B}{T_D - T_C} \right) \quad (1)
 \end{aligned}$$

This expression may be reduced to a more convenient form by substituting the expansion ratio r_e for $\frac{V_E}{V_D}$ and the compression ratio r_c for $\frac{V_B}{V_C}$.

For the adiabatic change BC

$$\frac{T_C}{T_B} = \left(\frac{V_B}{V_C} \right)^{k-1} = r_c^{k-1}$$

For the constant-pressure change CD

$$\frac{T_D}{T_C} = \frac{V_D}{V_C} = \left(\frac{V_D}{V_E} \times \frac{V_E}{V_C} \right) = \frac{r_e}{r_c}$$

Note that $V_B = V_E$; hence multiplication of $\frac{V_D}{V_C}$ by $\frac{V_B}{V_E}$ does not change its value.

For the adiabatic expansion DE

$$\frac{T_E}{T_D} = \left(\frac{V_D}{V_E} \right)^{k-1} = \frac{1}{(r_e)^{k-1}}$$

By dividing both numerator and denominator of the fraction in Equation (1) by $(T_D) \times (r_e)$ and multiplying the second term of the numerator by $\frac{T_C}{T_C}$, we have

$$\begin{aligned}
 \eta &= 1 - \frac{1}{k} \left[\frac{\frac{T_B}{T_D} \times \frac{1}{r_s} - \frac{T_C}{T_D} \times \frac{T_B}{T_D r_s}}{\frac{1}{r_s} - \frac{T_C}{T_D} \frac{1}{r_s}} \right] \\
 &= 1 - \frac{1}{k} \left[\frac{\frac{1}{(r_s)^{k-1}} \times \frac{1}{r_s} - \frac{1}{(r_s)^{k-1}} \times \frac{r_s}{r_s} \times \frac{1}{r_s}}{\frac{1}{r_s} - \frac{r_s}{r_s} \frac{1}{r_s}} \right] \\
 &= 1 - \frac{1}{k} \left[\frac{\frac{1}{(r_s)^k} - \frac{1}{(r_s)^k}}{\frac{1}{r_s} - \frac{1}{r_s}} \right]
 \end{aligned}$$

The work of an ideal Diesel cycle, air standard, may be determined as follows

- 1 The net value of the work done during processes AB and BA is zero
- 2 The net work of the cycle is represented by the closed area $BCDF$. Geometrically this area is equal to the area under CDE less the area under BC
- 3 Analytically this reduces to the work done during expansion CD plus the work done during expansion DE , minus the work done during compression BC , i.e.

$$W_{\text{net}} = {}_C W_D + {}_D W_E - {}_B W_C$$

Since CD is a constant-pressure expansion

$${}_C W_D = p_C (V_D - V_C)$$

For the adiabatic expansion DE

$${}_D W_E = \frac{p_E V_E - p_D V_D}{1 - k}$$

For the adiabatic compression BC

$${}_B W_C = \frac{p_C V_C - p_B V_B}{1 - k}$$

Example

The pressure and temperature at the beginning of compression in a Diesel engine cylinder are 18 lb per sq in. abs and 200°F respectively. The volume at this point is 2.4 cu ft and the compression ratio is 12 to 1. The volume increase during the burning of the fuel is 80%. The engine operates at 200 rpm. On the air-standard basis and with $k = 1.4$, calculate the horsepower developed per cylinder and the temperature at the end of compression.

Solution

In terms of the diagram (Fig. 7-8)

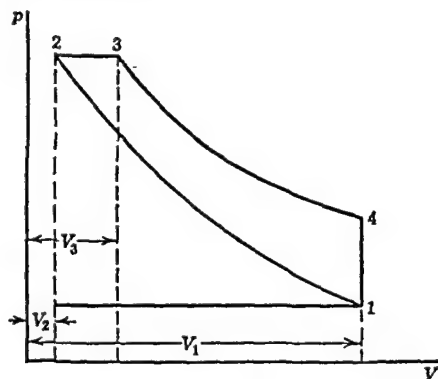


FIG. 7-8.

$$\begin{aligned} p_1 &= 18 \text{ lb per sq in. abs} \\ T_1 &= 200 + 460 = 660^\circ \text{ R} \\ V_1 &= 2.4 \text{ cu ft} \end{aligned}$$

The compression ratio is 12 to 1, so

$$\begin{aligned} \frac{V_1}{V_2} &= 12 \quad \text{and} \quad V_2 = \frac{2.4}{12} \\ &= 0.2 \text{ cu ft} \end{aligned}$$

By air-standard assumptions, the compression 1 to 2 is adiabatic. Hence

$$\begin{aligned} p_1 V_1^k &= p_2 V_2^k; \quad p_2 = p_1 \left(\frac{V_1}{V_2} \right)^k = 18(12)^{1.4} \\ &= 583 \text{ lb per sq in. abs} \end{aligned}$$

$$\begin{aligned} \text{Work of compression} &= \frac{p_2 V_2 - p_1 V_1}{1 - k} \\ &= \frac{144(583 \times 0.2 - 18 \times 2.4)}{-0.4} \\ &= \frac{144 \times 73.4}{-0.4} = -26,400 \text{ ft-lb} \end{aligned}$$

$$V_3 = 1.8 \times V_2 = 1.8 \times 0.2 = 0.36 \text{ cu ft}$$

$$\begin{aligned} \text{Work of constant pressure expansion} &= p(V_3 - V_2) \\ &= 144 \times 583 \times 0.16 = 13,430 \text{ ft-lb} \end{aligned}$$

For the assumed adiabatic expansion 3-4

$$\begin{aligned} V_4 &= V_1, \quad p_3 = p_2, \quad p_3 V_3^k = p_4 V_4^k \\ \text{Then} \quad p_4 &= p_3 \left(\frac{V_3}{V_4} \right)^k = 583 \left(\frac{0.36}{2.4} \right)^{1.4} \\ &= 41.0 \text{ lb per sq in. abs} \end{aligned}$$

$$\begin{aligned}\text{Work of expansion 3-4} &= \frac{P_1 V_1 - P_2 V_2}{1 - k} \\ &= 144 \frac{(41 \times 2.4 - 553 \times 0.36)}{-0.4} \\ &= \frac{144(-110.5)}{-0.4} = 39,800 \text{ ft-lb}\end{aligned}$$

$$\begin{aligned}\text{Total work of expansion} &= {}_1W_2 + {}_3W_4 \\ &= 13,430 + 39,800 = 53,230 \text{ ft-lb}\end{aligned}$$

$$\text{Net work of cycle} = 53,230 - 26,400 = 26,830 \text{ ft-lb}$$

$$200 \text{ rpm} = 100 \text{ cycles per min per cylinder}$$

$$\text{hp per cylinder} = \frac{100 \times 26,830}{33,000} = 81.4 \text{ hp}$$

Temperature at end of compression

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{k-1} = 660 \times (12)^{0.4} = 1782^\circ \text{ R}$$

$$T_2 = 1782 - 460 = 1322^\circ \text{ F}$$

It has already been stated that the foregoing analyses, based on an *air-standard* assumption, are mere approximations. As a matter of fact, efficiencies determined by the air-standard analysis are from 10 to

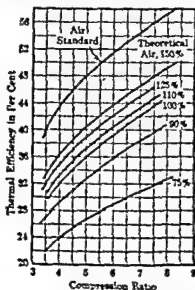


FIG. 7-9 Variation of Efficiency with Compression Ratio and with Mixture Strength for Otto Cycle

(From Univ. of Illinois Bull. No. 160, *A Thermodynamic Analysis of Internal Combustion Engines*, by G. A. Goodenough and J. B. Eaker, pp. 40, 41)

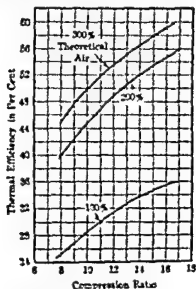


FIG. 7-10 Effect of Compression Ratio and Mixture Strength upon Efficiency of Diesel Cycle

25% higher than actual efficiencies. A comparison of air-standard efficiency with efficiencies accurately determined is shown by Figs. 7-9 and 7-10, which also show the effect of factors affecting efficiency.

Theoretical Analysis of Internal Combustion Engine Cycles

Both in the design of internal combustion engines and in fuel research it is necessary to study in minute detail what actually happens inside the cylinder. This means that a complete thermodynamic analysis of the cycle must be made. The purpose of such an analysis is to determine as nearly as possible the actual thermodynamic performance of the cycle under various compression ratios, with various fuels, and for various mixtures of fuel and air. With the Otto cycle attention must also be given to the effect of varying the ignition point. With the Diesel cycle the effect of variation in the time of beginning of fuel injection as well as the duration thereof must be studied. This type of analysis requires refined laboratory technique and considerable complicated calculation.

Even though a complete exposition of such an analysis is beyond the scope of this book, the authors do not wish to pass over it without referring to the admirable work which was done along this line by the late Professor George A. Goodenough and John B. Baker. Even in an accurate analysis certain assumptions are necessary. In order that the student may compare them with those of the air-standard analysis, they are given in the following list.*

1. The pressure of the mixture during the suction and exhaust strokes is the pressure of the atmosphere.
2. All the operations of the cycle are adiabatic. (This means that heat is added *only* by the combustion of the fuel *within* the cylinder and rejected *only* by the exhaust of the medium from the cylinder.)
3. The combustion is at constant volume in the Otto cycle and at constant pressure in the Diesel cycle.
4. In the case of liquid fuel, the fuel is completely vaporized before entering the cylinder.

For an accurate analysis, the following phenomena must be taken into account.†

1. The variation in the composition of the mixture during the phases of the cycle.
2. The variable specific heats of the various gaseous mixtures.
3. The dissociation of the products of combustion at high temperatures.

The following conclusions are verified by the Goodenough-Baker‡ analysis.

* G. A. Goodenough and J. B. Baker, *A Thermodynamic Analysis of Internal Combustion Engine Cycles*, Univ. of Illinois Bulletin No. 160.

† *Ibid.*

‡ *Ibid.*

- 1 The efficiency increases with the compression ratio, i.e., the higher the compression the higher the efficiency, other conditions remaining the same (See Figs 7-9 and 7-10)
- 2 For the same compression, the efficiency increases with increase in the percentage of air in the fuel mixture. A lean mixture gives a higher efficiency than a rich mixture.
- 3 The mean effective pressure, and therefore the power, is maximum when the air supply is somewhat less than 100% of the theoretical amount for complete combustion of the fuel in the mixture. Thus the mixture for maximum power is one of relatively low efficiency.
- 4 The ideal efficiencies obtained from the use of various liquid fuels are practically the same.
- 5 The efficiencies of Diesel cycle engines as a group range higher than the efficiencies of those operating on the Otto cycle. However, a comparison of the two efficiencies at the same compression ratio ($r = 8$) shows that the Otto cycle is inherently more efficient than the Diesel. The superior efficiency of the Diesel cycle in practice results from the high compression ratio that is permitted by its system of operation.

Empirical Formulas *

If the air standard formula derived for the ideal Otto cycle is given the general form $\eta = 1 - \frac{1}{(r)^\gamma}$, it may be used to determine the theoretical thermal efficiency. The determination of γ must then be based on the accurate system of analysis already mentioned, or be made from empirical formulas. Values of γ computed by Goodenough and Baker are given in the following tabulation.

VALUES OF EXPONENT γ

Compression Ratio % Air Supplied \rightarrow 100		110	125	150
3.5	0.2723	0.2723	0.3022	0.3189
5.0	0.2770	0.2916	0.3055	0.3214
6.5	0.2802	0.2942	0.3075	0.3232
8.0	0.2815	0.2964	0.3087	0.3248

These values of γ check quite accurately with values obtained from the empirical formula

$$\gamma = 0.3867 - \frac{6.5}{a - 35} - \frac{0.043}{r}$$

a = percentage of theoretical air supplied

r = compression ratio

When air supply is insufficient for complete combustion, the empirical formula

$$\gamma = 0.524 - \frac{24.6}{a}$$

gives a fair approximation of γ . The same formula

$$\eta = 1 - \frac{1}{(r)^\gamma}$$

may be used to determine ideal efficiency for the Diesel cycle when the value of γ is obtained from the empirical formula

$$\gamma = 0.434 - \frac{19.5}{a - r} - \frac{0.7}{r}$$

in which a and r denote the same quantities as before.

The ideal thermal efficiency determined by these empirical methods indicates the maximum amount of *available energy* for an internal combustion engine cycle operating under specific conditions, just as the Carnot cycle gives the maximum available energy for any reversible heat cycle operating between two given temperatures. It follows that comparison of ideal efficiency with actual efficiency, as obtained by comparison of shaft output with the heating value of the fuel consumed, offers a most enlightening study of engine performance.

Before leaving this subject, some consideration must be given to the influences that bring about the discrepancy between *shaft output* and *available energy*. The examples of actual indicator diagrams given in Figs. 7-3 and 7-4 (page 223) show clearly that in the actual engine the intake pressure along path AB drops *below* atmospheric pressure and that the pressure along path BA is *above* that of the atmosphere. This variation from the ideal involves an expenditure of energy referred to as "pumping loss." Inefficient combustion of the fuel and the internal cooling effect of moisture in the air supply cause a loss of availability in that they reduce the effectiveness of energy transformation. There is a necessary loss of energy in the heat rejected to the water jacket in order that the metal of the cylinder walls will not become so hot as to cause distortion.* An exhaust pressure above that computed for the ideal cycle, with resultant higher temperature of the products of combustion at rejection, means less energy transformed into work during the expansion stroke. Ever-present mechanical friction adds further to the amount of dissipated energy.

* Some investigators contend that a large portion of this heat would leave the cycle in any event during the exhaust stroke and is therefore really part of the inherently unavailable energy.

The modern tendency is to view internal combustion engine efficiency in terms of the result obtained by comparing actual brake efficiency with ideal thermal efficiency. In this way the energy which must be unavoidably wasted in accordance with the Second Law of Thermodynamics is not charged to the engine. Consequently, attention is focused directly on the practical problem of reducing the effect of those influences which tend to dissipate *available energy*.

PROBLEMS

- 1 Trace the Otto cycle and Diesel cycle on both the pV and TS diagrams and discuss in detail the changes around the cycle. Compare with the Carnot cycle. State the industrial uses to which these two cycles are adapted.
- 2 Why is the fuel in the Otto cycle burned at constant volume while in the Diesel cycle it burns at constant pressure? What are the advantages of each?
- 3 State the assumptions made in computing air standard efficiency of an internal combustion engine. Compare air standard efficiency with the correct value.
- 4 A certain Diesel engine transforms 38% of the heat supplied into work. If 1 lb of oil has a heating value of 19 000 Btu, what is the oil consumption per hour of a 400 hp engine? 1 hp-hr = 2545 Btu.
- 5 Sketch the Otto cycle on both pV and TS diagrams. State in detail how you would proceed in determining the net work of the cycle on the air standard basis, given the *intake pressure and temperature*, the *clearance volume* and *fuel*, the *displacement volume*, the *mass of fuel burned per cycle* and the heating value of the fuel.
- 6 What are the advantages of the internal combustion engine? Its disadvantages? Name the four strokes in the four stroke-cycle engine. What causes the explosive mixture to enter the cylinder? What is meant by the statement that the mixture in a gas engine is "too rich" or "too lean"?
- 7 How does the temperature of the gaseous products of combustion in the cylinder of a gas engine at the moment of ignition compare with the temperature at the moment of exhaust? Explain.
- 8 A Diesel engine cylinder has a volume of 4 cu ft and a compression ratio of 12 to 1. The volume at fuel cutoff is $\frac{1}{2}$ cu ft. Pressure at the beginning of compression is 15 lb per sq in. abs. Using a value of $k = 1.4$ for the adiabatic compression and expansion, determine on the air standard basis the theoretical horsepower developed at 200 rpm.

Steam Cycles, Steam Engines and Turbines

Introduction

At about the same time that the American colonies were winning their independence from Great Britain, James Watt and others devised the steam engine, the first practical apparatus for transforming heat energy into mechanical energy. Great as have been the consequences of the American Revolution in world politics, the development of the use of steam as a thermodynamic medium has brought about far more profound changes in the character of civilization itself. Through its use, man has multiplied the power at his disposal many thousandfold. The availability of power for industrial use is the prime factor that made possible the development of our present machine age. The machines in the factories of every modern industry become just so much metal when the power supply is shut off. In homes and offices, public buildings and movie palaces there is the same dependence upon an uninterrupted power supply. And all this began with the use of steam as a medium for transforming heat into mechanical energy.

Today, power is made available in steam, hydroelectric, and internal combustion engine plants. These three now have so many overlapping functions that it is difficult to say what their future relative importance will be. There is as yet nothing to indicate that the use of steam as a medium for transforming the chemical energy of fuels into mechanical power will be shoved into the background. The abundance of fuels suitable for use in the steam plant and the common occurrence of water make it seem likely that steam will be an important thermodynamic medium for many years to come.

The study of thermodynamics is frequently presented in terms of elementary steam engineering. While open to serious criticism, this view receives some justification in the fact that the steam engine was the first practical application of thermodynamics. Certain it is that every engineering student should understand the relationship of basic thermodynamic principles to steam engineering. But the science of thermodynamics is actually so broad that it should not be considered

as merely a means of explaining the operation of a steam plant. Hence the purpose of this chapter is to relate steam engineering to thermodynamics, rather than to submerge thermodynamics in a detailed study of the steam cycle.

Equipment of the Steam Power Plant

The *simple steam plant* includes the following essential equipment.

- 1 A furnace or firebox in which the combustion of fuel provides a source of heat
- 2 A boiler in which water is warmed and evaporated. The function of the boiler may also be extended to include superheating the vapor.
- 3 A prime mover (engine or turbine) through which the steam expands and delivers external mechanical work.
- 4 A condenser (the cold body) to which the expanded steam is exhausted and condensed and in which unavailable heat is rejected.
- 5 A hot well tank which receives the condensed steam or condensate.
- 6 A feed pump to pump water into the boiler.
- 7 Connecting pipe lines.

Fig. 8-1 is a schematic diagram of the way these items of equipment are arranged. A plant possessing this equipment operates on a closed cycle, i.e., the medium remains in the system. In some cases in which

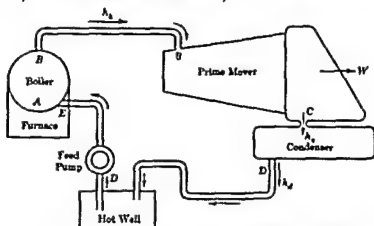


FIG. 8-1 Schematic Diagram of the Arrangement of a Simple Steam Power Plant.

the engine is a reciprocating one, the plant operates on an open cycle, i.e., the expanded steam is exhausted to the atmosphere. This arrangement does not alter the essential character of the cycle, although it does influence the back pressure on the engine and requires a continuous new supply of feed water. It is not practical to operate a steam turbine without the use of a condenser.

The ideal cycle of the plant illustrated is called the Rankine cycle. As a matter of fact, this cycle has been generally replaced in large modern plants by more complicated cycles of higher efficiency. However, for the sake of simplicity, our immediate objective will be to analyze the Rankine cycle as a basis for the thermodynamic study of other steam cycles.

The Ideal Rankine Cycle

During either evaporation or condensation, pressure is a function of temperature only. Consequently, constant-pressure evaporation, which can be easily achieved in a boiler, is also an *isothermal expansion*. Likewise, constant-pressure condensation, also readily achieved in a condenser, is an *isothermal compression*. Under ideal circumstances, we may assume that expansion in an engine* is both reversible and *adiabatic*. Consequently, when a wet or saturated vapor such as steam is used as a medium, it is possible to set up an ideal cycle in which three of the four processes of the Carnot cycle are present. The fourth process, reversible adiabatic compression, cannot be realized practically and so for this process the Carnot cycle must be modified as described in the following

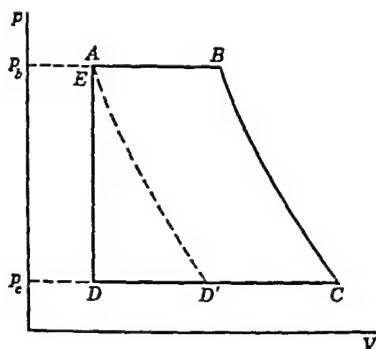


FIG. 8-2. Rankine Cycle and Comparison with Carnot Cycle on the pV Diagram.

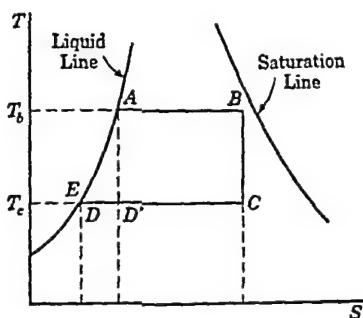


FIG. 8-3. Rankine Cycle and Comparison with Carnot Cycle on the TS Diagram.

paragraph. The resulting cycle, thus modified, is called the Rankine cycle in honor of the Scottish engineer of that name.

Figs. 8-2 and 8-3 show the Rankine cycle on the pV and TS diagrams respectively by $ABCDEA$. For comparison, a Carnot cycle operating under similar conditions is indicated by $ABCD'A$. Point A represents the state of a saturated liquid at boiler pressure p_b . Isothermal addition of heat during evaporation in the boiler is represented by AB . Reversible

* The term engine as used in this discussion may be construed to include either reciprocating engines or turbines unless otherwise stated.

boiler is wet. BC represents adiabatic expansion in the engine, with resulting delivery of external mechanical work. CD indicates the condensation of the vapor in the condenser at the constant pressure p_c . DE represents the change in state of the liquid as it is pumped into the boiler, with accompanying increase of pressure from p_c to p_b . Points D and E are nearly coincident. Point E represents the state of saturated liquid immediately after it has been pumped into the boiler. At this point its temperature is that of the condenser t_c , and its pressure is boiler pressure p_b . The difference in energy of the medium between these two points is the change in enthalpy from h_d to h_e resulting from the flow work done on the medium. During the process, both temperature and specific volume remain constant. Hence there is no change in intrinsic energy and

$$h_e - h_d = v_D(p_b - p_c)$$

This change in enthalpy is so small in comparison with other energy changes around the cycle that it is ordinarily neglected in computing Rankine efficiency. For example, with a boiler pressure of 210 lb per sq in. abs and a condenser pressure of 10 lb per sq in. abs

$$v_D = 0.019 \text{ cu ft}$$

$$\text{and } h_e - h_d = \frac{0.019 \times 144(210 - 10)}{778} = 0.7 \text{ Btu per lb approx}^*$$

In order to determine the thermal efficiency of the Rankine cycle let us start with a general expression for efficiency, i.e.

$$\eta_R = \frac{\text{heat supplied (in the boiler)} - \text{heat rejected (in the condenser)}}{\text{heat supplied (in the boiler)}}$$

Since the heat supplied in the boiler during processes EA and AB is at the same constant boiler pressure p_b , its amount is measured by the change in enthalpy, $h_b - h_e$. Similarly, the heat rejected in the condenser at constant pressure p_c is measured by $h_c - h_d$.

$$\text{Then } \eta_R = \frac{(h_b - h_e) - (h_c - h_d)}{h_b - h_e}$$

If the difference between h_e and h_d is neglected as suggested previously, h_d may be substituted for h_e and the expression may be written

$$\eta_R = \frac{(h_b - h_d) - (h_c - h_d)}{(h_b - h_d)} = \frac{h_b - h_c}{h_b - h_d}$$

This equation shows that the work of a Rankine cycle is given by

$$\text{heat supplied} - \text{heat rejected} = h_b - h_c$$

* For very high-pressure boilers the quantity $h_e - h_d$ may be large enough to require consideration.

Since the delivery of work takes place during the reversible adiabatic expansion BC , the student may at first think that the work of the change should be measured by change of intrinsic energy rather than by change of enthalpy. The question is cleared up at once when it is realized that

$${}_1W_2 = -\Delta E \text{ for a non flow adiabatic change}$$

In the Rankine cycle, vapor is continually admitted and exhausted from the engine. Consequently, the adiabatic expansion is a part of the f_0 process during which the work done is properly measured by change in enthalpy.

Example

In a certain steam plant the boiler is operated at a pressure of 300 lb per sq in. gage. A vacuum gage on the condenser reads 15 in. of mercury. The barometer reads 29 in. of mercury. A throttling calorimeter test of the steam in the main steam line shows its quality to be 0.96. From indicator cards taken on the engine cylinders the indicated horsepower is computed as 250 hp. The steam consumption is 3000 lb per hr. (a) Compute the ideal Rankine cycle efficiency of the plant. (b) Compare this with the efficiency of a Carnot cycle operating between the temperature of evaporation of water in the boiler and the condenser temperature. (c) Compute the energy loss per pound of steam between the boiler and engine.

Solution

It is first necessary to determine the absolute pressure in the boiler and condenser.

$$\text{Atmospheric pressure} = 29 \times 0.491 = 14.2 \text{ lb per sq in. abs}$$

$$\text{Boiler pressure} = 300 + 14.2 = 314.2 \text{ lb per sq in. abs}$$

$$\text{Condenser pressure} = (29 - 15) 0.491 = 6.87 \text{ lb per sq in. abs}$$

(a) Rankine efficiency

$$\eta_R = \frac{h_2 - h_3}{h_2 - h_4}$$

The several values of enthalpy in this equation may be determined from either the saturated steam tables or the Mollier chart. From the saturated steam tables (see Chapter 5)

$$h = h_f + xh_{fg}$$

and for the boiler pressure, 314.2 lb per sq in. abs

$$h_2 = 398.5 + 0.96 \times 804.2 = 1170.5 \text{ Btu per lb}$$

This value may be checked on a Mollier chart by reading the value of h for point B on Fig. 8-4. The reversible adiabatic expansion BC is characterized by constancy of entropy. If, from point B , a constant-entropy line is followed to its intersection with the constant pressure line corresponding to 6.87 lb per sq in. or 14 in. of mercury (condenser pressure), the state point C of the steam entering the condenser is established. From the chart, the quality at this point

is 0.777, and h_c equals 915 Btu per lb. The value of h_c may also be determined by means of the tables in accordance with the method in Chapter 5.

To determine x_c , we use the fact that $s_b = s_c$.

$$s_b = s_f + x_b s_{fg}$$

For the pressure, 314.2 lb per sq in. abs

$$s_b = 0.59355 + 0.96 \times 0.9127 = 1.46955$$

Also

$$s_c = s_f + x_c s_{fg}$$

For condenser pressure, 6.87 lb per sq in. abs

$$s_c = 0.2566 + x_c \times 1.5612$$

Since

$$s_b = s_c$$

$$1.46955 = 0.2566 + x_c \times 1.5612$$

$$x_c = \frac{1.46955 - 0.2566}{1.5612} = 0.778$$

Then

$$h_c = h_f + x_c h_{fg}$$

At condenser pressure, 6.87 lb per sq in. abs

$$h_c = 143.77 + 0.778 \times 992.24 = 915.7 \text{ Btu per lb}$$

From the tables h_d is obtained as the value of h_f for a saturated liquid at the condenser pressure of 6.87 lb per sq in. abs.

$$h_d = 143.77 \text{ Btu per lb}$$

Substitution in the expression

$$\eta_R = \frac{h_b - h_c}{h_b - h_d}$$

gives

$$\eta_R = \frac{1170.5 - 915.7}{1170.5 - 143.77} = \frac{254.8}{1026.7} = 0.248$$

$$\eta_R = 24.8\%$$

(b) The steam tables give the temperature of evaporation corresponding to a boiler pressure of 314.2 lb per sq in. abs as 422° F. The temperature corresponding to the condenser pressure, 6.27 lb per sq in. abs, is 176° F.

$$T_b = 422 + 460 = 882^\circ \text{ R}$$

$$T_c = 176 + 460 = 636^\circ \text{ R}$$

$$\eta_{\text{Carnot}} = \frac{T_b - T_c}{T_b} = \frac{882 - 636}{882} = \frac{246}{882} = 0.279$$

$$\eta_{\text{Carnot}} = 27.9\%$$

This figure shows that Rankine efficiency is surprisingly close to Carnot efficiency; in the example η_{Rankine} is 88.5% of η_{Carnot} . This gives the Rankine cycle the appearance of being highly efficient, and so it is for the temperature range involved. But because of the fact that the temperature range is restricted to the limits of practical boiler pressure, the steam cycle is characterized by low thermal efficiency. Further, as the boiler pressure and hence temperature T_b increase, the difference between Carnot efficiency and Rankine efficiency increases.

(c) The steam consumption per 1 hp-hr is

$$\frac{3456}{42.8} = 12 \text{ lb} \\ 12 \times (h_3 - h_2) = 12 \times 254.8 = 3060 \text{ Btu}$$

On the basis of the Rankine analysis this amount of energy is available for transformation for each 1 hp-hr actually delivered. Since 1 1 hp-hr is equivalent to 2545 Btu

$$3060 - 2545 = 515 \text{ Btu lost per 1 hp-hr delivered} \\ \text{or} \quad \frac{515}{12} = 42.8 \text{ Btu lost per lb of steam used}$$

Attention is directed to this loss here to emphasize the fact that the Rankine analysis takes no account of energy dissipated by conduction, radiation, etc. between the boiler and engine, whereas this loss cannot be wholly eliminated in practice.

The indicated thermal efficiency is

$$\frac{2545}{12(h_3 - h_2)} = \frac{2545}{12 \times 1026.7} = 0.207, \text{ or } 20.7\%$$

The overall indicated thermal efficiency is obtained by comparing the heat equivalent of an indicated horsepower hour with the heating value of the amount of fuel required to deliver an 1 hp-hr. This efficiency takes account of all energy losses, including the furnace loss, i.e., heat generated by the fuel combustion which never enters the medium. The overall efficiency of a plant like the one described here would normally be in the neighborhood of 15%.

Methods for Improving Rankine Efficiency

Although Rankine efficiency is not expressed directly in terms of temperature of heat addition and rejection as is Carnot efficiency, inspection of the diagram of the cycle (Figs. 8-2 and 8-3) reveals at once that Rankine efficiency actually is governed by temperature range. Consequently we may increase efficiency by decreasing the condenser temperature or by increasing the boiler temperature.

Decreasing the Condenser Temperature

Since pressure is a function of temperature only for a wet vapor, a decrease in condenser temperature is accomplished by decreasing the condenser pressure. A condenser is a tank with tight joints through which cooling water is circulated. The condenser vacuum or pressure below atmospheric, is maintained by the hot well pump. Hence, condenser pressure may be reduced by increasing the action of the hot well pump and by paying careful attention to the prevention of leaks in gland packing, in pipe connections, and in the condenser shell itself. With a relatively slight vacuum in the condenser, there is a steep gradient between the temperature of the condensate and that of the circulating water. As the pressure is reduced, the temperature of the

condensate is also reduced and the slope of the gradient becomes less. Hence, each pound of circulating water absorbs less heat and consequently, to maintain efficient condensation, the quantity of circulating water must be increased.

The effect of a decrease in condenser pressure on efficiency is best demonstrated by an example. Suppose the condenser pressure in the

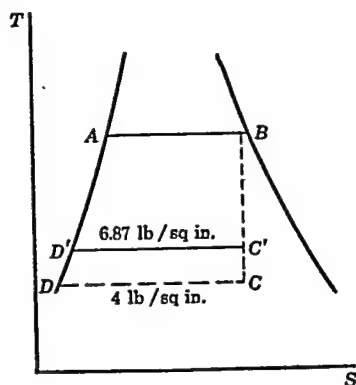


FIG. 8-5.

preceding example is reduced to 4 lb per sq in. abs, all other data remaining the same. (See Fig. 8-5.) At 4 lb per sq in. abs, $h_c = 888$ Btu per lb and $h_d = 121$ Btu per lb. Then

$$\eta = \frac{1170.5 - 888}{1170.5 - 121} = \frac{282.5}{1049.5} = 0.27, \text{ or } 27\%$$

Although lowering the condenser pressure is an effective means of increasing Rankine efficiency, a definite lower limit of pressure is imposed by the natural temperature of the circulating water available for cooling. This limit has been substantially achieved in modern practice with condensers that operate at an absolute pressure of about 1 in. of mercury. In this connection Sir Charles Parsons is said to have remarked some years ago, when discussing the changes in pressure required to improve the efficiency of steam plants, "There is only one thing for you to do. You cannot go down; you must go up."

Superheating

Steam temperature may be increased by superheating. This is accomplished by conducting the steam back through a coil of pipe in the furnace (a superheater) *after* it has been completely evaporated in the boiler proper. It then absorbs additional furnace heat, and since

it is beyond the saturated state, this addition of heat results in a temperature rise, even though the pressure remains constant. A Rankine cycle in which steam is delivered to the engine in a superheated state is shown on the TS and hS diagrams in Figs. 8-6 and 8-7 respectively.

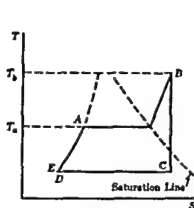


FIG. 8-6

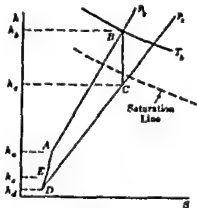


FIG. 8-7

To show the effect of superheating on Rankine efficiency, let us use for an example a cycle operating at the same boiler pressure (314.2 lb per sq in. abs) and condenser pressure (6.87 lb per sq in. abs) as in the preceding example. In the present case, let the steam be initially superheated to a temperature of 520° F. This represents an increase of 520 - 422 or 98° F in the temperature of the steam delivered. By means of the superheated steam tables or the Mollier chart we find that

$$h_b = 1267 \text{ Btu per lb}$$

$$h_c = 982 \text{ Btu per lb}$$

$$h_d = 143.8 \text{ Btu per lb}$$

$$\text{Then } \eta_R = \frac{h_b - h_c}{h_b - h_d} = \frac{1267 - 982}{1267 - 143.8} = 0.252, \text{ or } 25.2\%$$

This is a relatively slight increase in efficiency, even if the steam could be superheated to 1000° F, η would only reach approximately 29.6%. From these figures we may conclude that a curve showing Rankine efficiency versus temperature of superheat will be relatively flat. Consequently, superheating is *not* an effective means of improving thermal efficiency. In view of the increased range of the temperature drop during expansion through the engine, the ineffectiveness of superheating may at first appear startling. But when consideration is given to the fact that all of the heat of superheat is added while the medium is undergoing a sharp temperature rise and that only an incremental part is added at the highest temperature, the reason for this state of affairs becomes apparent. The increase in the entropy of the medium

that results from adding the heat in this manner is so great for the quantity added that the influence of the higher temperature attained is practically nullified.

However, superheating is not to be regarded as being without benefit because of the above fact. It has other results that are valuable. One important cause of energy dissipation in a steam cycle which is not taken into account in the Rankine analysis is fluid friction. This friction increases progressively as condensation sets in at the end of expansion. Moreover, the presence of water in the engine produces an undesirable scouring effect on the metal of the equipment. These effects are particularly significant in turbines where the velocity of the medium relative to that of the blades is extremely high. The presence of liquid also accelerates the loss of heat by conduction through the cylinder or turbine walls. Superheating either wholly prevents or at least delays the appearance of moisture during the passage of the medium through the engine or turbine. This may readily be observed by comparing the positions of line BC on the two hS diagrams in Figs. 8-4 and 8-7. Superheating also increases the energy carried per pound of steam. Consequently, the number of pounds of steam required per horsepower hour is less, and this makes possible a reduction in the size of the engine equipment for a given output.

For these reasons superheating is almost universally used in large modern plants. Temperatures of 650°F to 750°F are now common, and higher temperatures will unquestionably be employed as soon as metallurgical developments provide metals capable of withstanding them.

Increasing the Boiler Pressure

The discussion in this and other chapters has emphasized the fact that the most desirable feature of a heat cycle is to have a maximum part of the heat supplied to the medium isothermally and at the highest possible temperature. Since the temperature of evaporation increases progressively with increase in pressure, it is certain that increasing the boiler pressure must result in increased thermal efficiency of a Rankine cycle.

Let us consider a Rankine cycle in which approximately the same amount of heat is added as was added in the example on page 244. We shall use the data in that example, *except* for the boiler pressure, which will be taken here as 500 lb per sq in. abs. Then

$$p_b = 500 \text{ lb per sq in. abs}$$

$$p_c = 6.87 \text{ lb per sq in. abs}$$

$$\text{Initial quality} = 0.96 \text{ (see Fig. 8-8)}$$

From the Mollier chart

$$h_b = 1174 \text{ Btu per lb}$$

$$h_c = 890 \text{ Btu per lb}$$

$$h_d = 143.8 \text{ Btu per lb}$$

$$h_b - h_d = 1.8 \text{ Btu per lb} \quad \text{This may be neglected}$$

$$\eta_R = \frac{h_b - h_c}{h_b - h_d}$$

$$= \frac{1174 - 890}{1174 - 143.8}$$

$$= 0.276, \text{ or } 27.6\%$$

It is to be noticed that this cycle requires an increase in the energy supplied of only 3.5 Btu per lb over that in the example on page 245. Yet the increase in Rankine efficiency is 2.8%. If the boiler pressure were increased to 1000 lb per sq in. abs and the same condenser pressure were

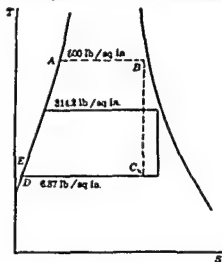


FIG. 8-8

used, the efficiency would be 31.2%. An even more pronounced improvement in efficiency will be observed if additional heat to carry the vapor near the saturation point is supplied, as would be the case in practice. Experience and investigation have always pointed to the effectiveness of increasing boiler pressure to increase thermal efficiency. The application of this idea has led from early boiler pressures less than 50 lb per sq in. to the present common use of boilers under pressures of from 400 to 600 lb per sq in. This progress has been made possible by the development of metallurgical processes which have provided metals and equipment capable of withstanding the effects of high pressure and temperature.

We should be remiss if we did not take this opportunity to suggest that the student refer to the example on page 82 in the discussion of entropy. It provides an alternative and helpful point of view from which the effect of raising the steam temperature may be considered. The energy delivered to the steam is withdrawn irreversibly from the hot products of combustion at the high furnace temperature. This irreversible heat flow results in an increase in the entropy of the energy, with a consequent decrease in its availability. The higher the average temperature of the medium, the less is the temperature gradient and the less is the increase in the entropy of the energy. As a result, the availability of the energy delivered to the medium is greater the more nearly its temperature, on entering the medium, approaches that of the furnace.

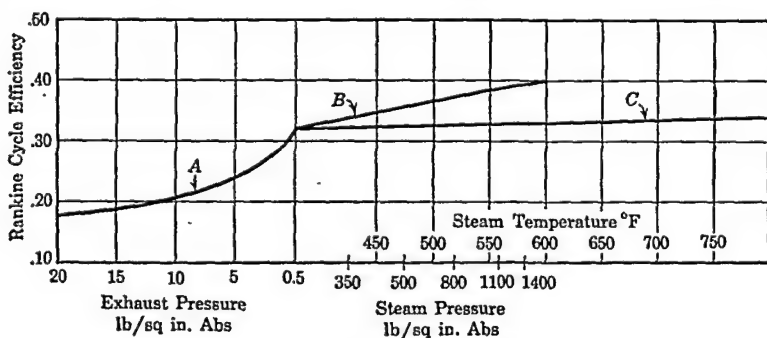


FIG. 8-9.

Increase in Rankine Efficiency. (A) With reduction in condenser pressure; (B) with increase in boiler pressure without superheat; (C) with superheat (constant pressure). (Reprinted by permission from *Principles of Engineering Thermodynamics*, by Kiefer and Stuart, published by John Wiley & Sons, Inc.)

In order to illustrate further the relative effectiveness of the three means of improving Rankine efficiency, a set of curves is shown in Fig. 8-9. In evaluating the analysis of a Rankine cycle we must remember that it has been treated as an ideal cycle. In real plants actual efficiency is influenced by ever-present losses due to turbulence, throttling, heat conduction, friction, and the like.

Improvements in Efficiency Outside the Rankine Cycle

Although increasing the boiler pressure may appear to offer the best opportunity for improving steam plant performance, steam engineers have not overlooked other possibilities. They have carried their investigation outside the Rankine cycle, constantly seeking improvements which would reduce the fuel cost per unit of power delivered. So intense has been this campaign that over the period of the last twenty years utility companies throughout this country as a whole have been

able to reduce coal consumption per kilowatt hour by approximately 50%. Much of this saving may be assigned to boiler and turbine improvements and to reduction of general losses. However, an appreciable part has resulted from the adoption of cycles which possess inherent advantages over the Rankine cycle. The *regenerative feed heating cycle* and the *reheating cycle* or a combination of the two embody the present trend in steam plant design. The *binary cycle*, though in use in a few plants in this country and abroad, has not yet passed the developmental stage and its ultimate general adoption is somewhat doubtful.

Regenerative Feed Heating Cycle

The departure of ideal Rankine efficiency from Carnot efficiency is a result of the manner in which heat is added along the path $E4$ (Fig. 8-3). This process is accompanied by a growth in entropy not encountered in a Carnot cycle. In the actual Rankine cycle there is also an increase in entropy occasioned by the irreversible mixing of the relatively cool

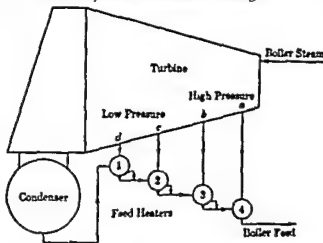


FIG. 8-10 Arrangement for Four-Stage Regenerative Feed Heating

feed water with the relatively hot water in the boiler. The effect of such an irreversible mixing process is illustrated in the example on page 81.

The regenerative feed heating cycle has as its objective the reduction of these undesirable influences. Their complete elimination would be accomplished only if the process EA could be made reversible. In theory, regenerative feed heating may bring about an approach to this limit, but the multiplicity of devices required prevents its attainment in practice. A considerable improvement in thermal efficiency can be obtained, however, by a limited number of regenerative feed heating stages. The design and size of the steam plant dictate the number of heaters which can be economically employed. Two heaters are com-

monly used in smaller plants, and three and four in larger installations. Fig. 8-10 shows a schematic arrangement for four-stage regenerative feed-heating.

To carry out this process of feed water heating, steam is bled from the turbine at successive stages of pressure. This steam is supplied to the feed heaters as indicated in the diagram. The condensate from the main condenser passes to the first heater (No. 1), where condensation of the steam bled from stage (*d*) of the turbine provides the heat necessary to raise the water to a saturated liquid at a pressure p_1 . With a progressive increase in pressure the liquid passes to each successive heater where it is heated to the saturated liquid point at the heater pressure. The condensate of the bled steam used in each heater also passes to the succeeding heater as feed water. By design and operation it is intended that just enough steam shall be bled and supplied to each heater so that the feed water will leave the heater as a saturated liquid at the pressure of the bled steam.

If this regenerative feed-heating could be carried out in an infinite number of stages, the temperature of the bled steam in each stage would need to be only an incremental amount higher than the temperature of the water entering the heater. Thus an isothermal reversible transfer of heat from steam to water would be approached. In the limit the feed water may be conceived as returning to the boiler as a saturated liquid at boiler pressure, that is, at state point *A* (Fig. 8-3). Further, the warming would have been accomplished by a series of reversible iso-

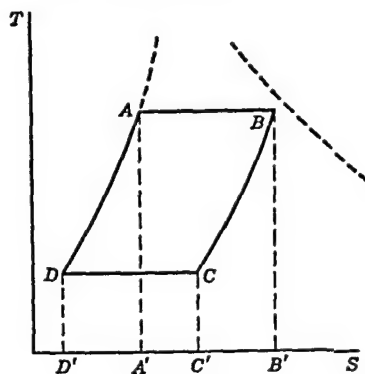


FIG. 8-11.

thermal processes and the cycle made to approach Carnot efficiency. The *TS* diagram of the cycle would be as shown in Fig. 8-11. Area *BB'C'C* represents the heat supplied by the bled steam, and area *AA'D'D* represents the same quantity of heat supplied to the feed water.

A cycle employing four stage heating as outlined above would appear on a TS diagram as indicated by Fig 8-12. Areas $a, b, c,$ and d represent the heat obtained from the steam bled at points $a, b, c,$ and d (Fig 8-10) and areas 1, 2, 3 and 4 represent the heat supplied to the feed water in each successive heater.

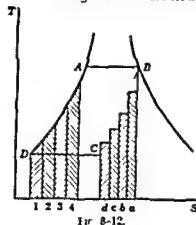


Fig 8-12.

Because of the withdrawal of steam at various stages of expansion in the turbine, more pounds of steam are required per horsepower delivered. Nevertheless, the utilization of the steam withdrawn for heating the feed water effects an improvement in thermal efficiency over the Rankine cycle. A

typical example using three stage feed heating discloses the following approximate comparative results

	Ideal Rankine Cycle	Ideal Regenerative Feed Heating Cycle
Pressure of steam entering turbine	300 lb per sq in abs	300 lb per sq in abs
Temperature of steam entering turbine	520° F	520° F
Steam per 1 hp-hr	6 lb	7 lb
Steam passing to condenser	6 lb	5.3 lb
Heat supplied via boiler and superheater	1220 Btu per lb	965 Btu per lb
Thermal efficiency	34.3%	37.5%

Reheating and Reheating Regenerative Cycles

Steam plants using superheated steam at high initial pressure offer the possibility of improvement outside the Rankine cycle by reheating the steam between pressure stages in the turbine. This is accomplished by returning the steam to the boiler for resuperheating after partial expansion in the high pressure section of the turbine. After reheating the expansion is completed in a lower pressure section of the turbine. The TS diagram of a reheating cycle is shown in Fig 8-13. Expansion

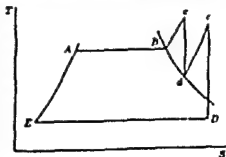


Fig 8-13

(*cd*) will ordinarily be carried initially to or near the saturation point. Reheating is represented by the path *dc'* and the final expansion carried out is indicated by *c'D*. The additional heat supplied during process *dc'* is of some significance, as is indicated by the diagram. However, the important advantage is the decrease in condensation coupled with the delay in its occurrence. This effect is particularly significant in turbines where the presence of liquid is most harmful.

A combination of reheating and regenerative feed water heating is customary in plants where reheating is employed. In this arrangement the first feed heater usually draws its steam from the line returning the steam to the reheater. Subsequent heaters are supplied with steam bled after the reheated steam has partially completed its expansion. Some indication of the effectiveness of this combination type of cycle may be gained from the curves shown in Fig. 8-14.*

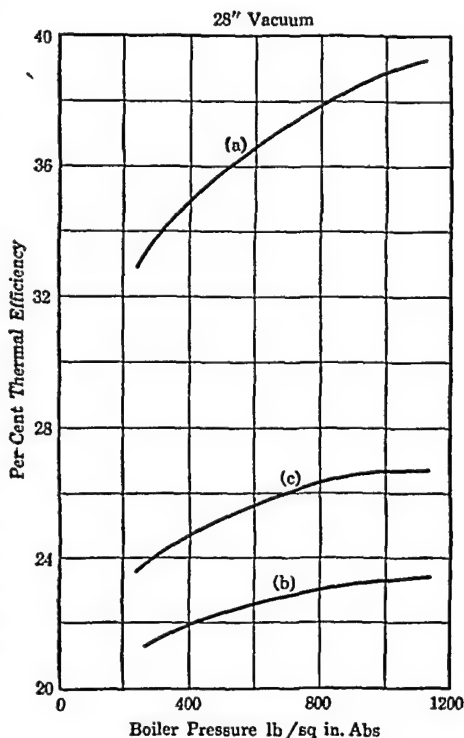


FIG. 8-14.

- (a) Maximum ideal Rankine cycle efficiency.
 (b) Overall plant efficiency with Rankine cycle.
 (c) Overall plant efficiency with reheating-regenerative cycle. (From A. H. Law and J. P. Chittenden, "Higher Steam Pressures and Their Application to the Steam Turbine," *Journal of the Institute of Electrical Engineers*, vol. 66, p. 94.)

Binary Cycles †

Raising the upper temperature of steam cycles by progressive increases in boiler pressure has not been accomplished without difficulties, and further efforts to increase pressures are

likely to create new and intricate problems. Recent experiments have indicated serious difficulties arising from the high velocity that accompanies evaporation at very high pressure. A tendency for the water vapor to dis-

* A. H. Law and J. P. Chittenden, "Higher Steam Pressures and Their Application to the Steam Turbine," *The Journal of the Institute of Electrical Engineers*, 66: 94, January, 1928.

† Gustaf A. Gaffert, "High-Pressure Steam and Binary Cycles as a Means of Improving Power Station Efficiency," *Trans. A.S.M.E.*, 56: 755, 1935.

sociate and form free gases, with resultant new deteriorating effects on metals, has also been observed. It is not surprising, then, that consideration has been given to the possibilities of employing media which evaporate at a high temperature and a relatively low pressure. Such media are available, but their use singly does not meet the necessary requirements because they also condense at relatively high temperature at ordinary condenser pressure. However, the possibility of combining two cycles using different media does have potentialities. In principle, the binary cycle involves the following:

- 1 Use of a "top" fluid whose vapor temperature is relatively high at about 200 to 300 lb per sq in. pressure.
- 2 Use of a "lower" fluid which will evaporate at suitable pressure at a temperature below the condenser temperature of the top fluid.
- 3 Evaporation of the "top" fluid in a boiler and expansion of the vapor through a turbine.
- 4 Use of the "top" fluid condenser as a heat exchanger to evaporate the "lower" fluid.
- 5 Superheating and expansion of the "lower" fluid through a second turbine. Condensation of the "lower" fluid in an ordinary water-cooled condenser.

Water appears as the logical "lower" fluid which satisfies all the requirements nicely. A satisfactory "top" fluid must, in general, satisfy the following conditions, as pointed out by Gaffert *:

- 1 The vapor pressure curve must be such that reasonable pressures, perhaps not over 300 lb per sq in., obtain at highest operating temperatures.
- 2 The critical temperature should be well above any possible desirable upper limit of temperature for cycle operation.
- 3 The vapor pressure at a desirable condensation temperature should be nearly atmospheric or at least not so low as to require excessive power for maintenance of vacuum.
- 4 The specific heat of the liquid should be low relative to water.
- 5 The fluid should not be costly and should be obtainable in reasonably large quantities.
- 6 The fluid should have no corrosive action upon metals ordinarily employed in power generation practice.
- 7 The fluid should not be poisonous or toxic and thereby endanger human life.
- 8 The freezing point of the fluid should be well below ambient room temperature.
- 9 The fluid should be stable under conditions of cycle operation at elevated temperatures.
- 10 The vapor condition after expansion through a turbine should be nearly saturated so that a reasonable coefficient of heat transfer will obtain.

* *Ind.*, 255

Of the fluids which have received consideration as "top" fluids — namely, aluminum bromide, zinc-ammonium chloride, mercury diphenyl and diphenyloxide — only mercury may be said to come safely within all of the requirements.

Several plants that use a mercury-water binary cycle are in operation in this country. From a thermal efficiency standpoint their existence is amply justified. The world's production rate of mercury places one definite limitation on the extent to which this cycle may be generally adopted. Other economic factors that are involved put the mercury-

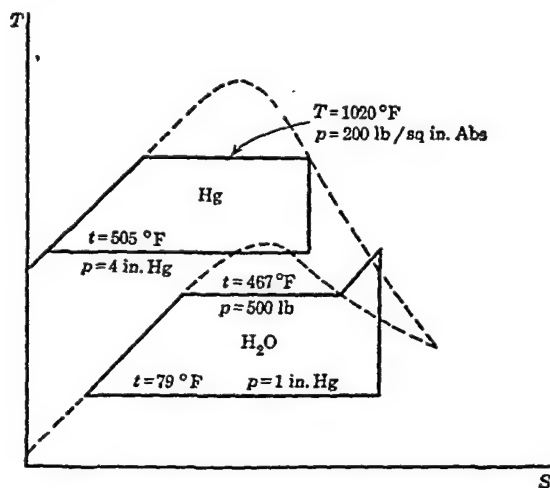


FIG. 8-15. Mercury-Water Binary Cycle.

water binary cycle in a very specialized field. Possibly some other fluid will be found that will solve the problem of the binary cycle more satisfactorily. Doubtless the possibilities have not yet been fully explored.

Fig. 8-15 shows the representation of a mercury-water binary cycle on the TS plane. Because of the specific heat relationship, this cycle requires an approximate ratio of 9 lb of mercury to 1 lb of water in circulation.

The Reciprocating Steam Engine

Although it is not the purpose of this chapter to discuss in detail the various mechanisms of the steam cycle, some consideration must be given to the processes which take place in the engine. The reciprocating engine and the turbine are the devices used in the steam cycle to convert a part of the available energy into shaft work. The conception of the theory of the turbine antedates that of the reciprocating engine by many years, although the latter was the first to be developed commercially.

The reciprocating engine was invented in the latter part of the eighteenth century by James Watt, an event that marked the beginning of the industrial era. Only within the last quarter century has the turbine largely displaced it in industrial importance.

The conventional modern reciprocating steam engine is of the double-acting, multiple-expansion, multi-cylinder type. In a double-acting engine steam is admitted alternately on both sides of the piston. The multiple-expansion engine involves carrying out the expansion

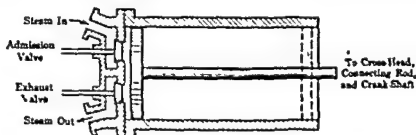


FIG. 8-16 Conventional Steam Cylinder and Valve Head.

from boiler to condenser pressure in a series of stages, each stage of expansion taking place in one or more cylinders. For the basic analysis only one single-acting cylinder need be considered. Essentially, a simple engine must consist of a cylinder, a cylinder head with suitable admission and exhaust valves, a piston and the necessary piston rod, crosshead, connecting rod, and crankshaft (see Fig. 8-16).

The two extremes in cycle operation of the engine are the non-expansion and complete-expansion engines. In the non-expansion engine, steam is admitted during the entire piston stroke, thus giving the effect of a constant-pressure flow process. At the end of the stroke the exhaust port is uncovered and the cylinder pressure drops quickly as the steam rushes out. Ordinarily this type of engine, which has some application in certain types of pumps, steam hammers, and similar devices, exhausts to the atmosphere.

The return stroke of the piston removes the residue steam from the cylinder. Neglecting clearance, we may represent the cycle of such an engine by a diagram like that shown in Fig. 8-17. The net work of the cycle is clearly

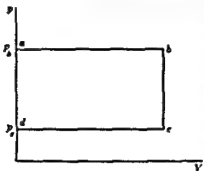


FIG. 8-17

$$M(p_a - p_c) = V_s(p_a - p_c)$$

where p_b and p_c are admission and condenser (or atmospheric) pressure respectively, and V_b is the volume swept through by the piston. This cycle delivers maximum power for a given piston stroke. It is least economical from the standpoint of steam consumption per unit of power because no useful effect is obtained by the pressure drop from b to c .

The cycle of operation for a complete-expansion engine (clearance being neglected) is represented on a pV diagram by Fig. 8-18. In such an engine the admission valve must close at a point b (called the point of cutoff) so that expansion to condenser pressure p_c will be complete at the end of the piston stroke. Such complete expansion requires a piston stroke of impractical length. Furthermore, beyond the point r , the work gained is offset by mechanical friction and no net useful effect

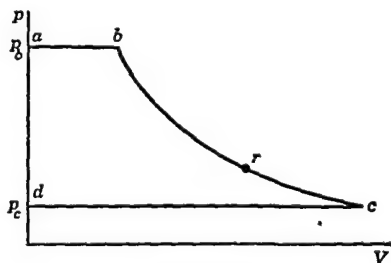


FIG. 8-18.

is obtained. For these reasons the complete-expansion cycle is not used in practice. For purposes of comparison in the discussion to follow, it is pertinent to notice how the work of this engine cycle may be evaluated. Reversible adiabatic conditions are assumed for the analysis. The work during process ab equals $p_b V_b$. For the adiabatic expansion bc the work equals $E_b - E_c$. For process cd the work equals $p_c V_c$. Hence the net work equals

$$p_b V_b + (E_b - E_c) - p_c V_c = M[(p_b v_b + e_b) - (p_c v_c + e_c)] \\ = M(h_b - h_c)$$

where h_b is the enthalpy of the admission steam and h_c is the enthalpy of the steam entering the condenser.

Let us view the whole process, $abcd$, as a flow process, which is actually the case when the engine is considered as an integral part of the entire steam cycle. We then see that the above analysis is in accord with the general proposition that for a *reversible adiabatic flow process with negligible change in velocity the external work done is measured by the change in enthalpy of the medium*.

The Incomplete-Expansion Cycle

The practical cycle for reciprocating steam engines lies between the two extremes discussed above and is applied in the incomplete-expansion engine. Actual engines must have a clearance space between the cylinder head and piston. The exhaust valve is set to close early so that steam

in the clearance space will be compressed to approximately the state of admission steam. The compression of this steam during the latter part of the exhaust stroke serves to cushion the reciprocating masses. It also raises the temperature of the metals and thus reduces condensation during the initial part of the stroke. An actual indicator diagram for one end of an engine cylinder is shown in Fig. 8-19. The net work of the engine may be determined from such a diagram by ascertaining the mean effective pressure as outlined on page 223 and using the expression $W' = p_m L A \lambda$.

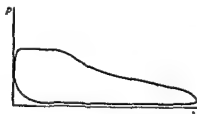


FIG. 8-19

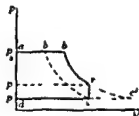


FIG. 8-20

Complete analysis of a reciprocating engine cycle involves consideration of the influence of the steam left in the clearance space, as well as of the effects of throttling, condensation, and reevaporation during the engine's cycle of operations. Since such an analysis is beyond the scope of this book, in order to simplify the discussion of principles involved we shall use an ideal cycle with adiabatic expansion and no clearance, as depicted in Fig. 8-20.

With the exhaust port closed, steam is admitted at a constant pressure p_a during process ab . The admission valve closes at b , the point of cutoff. Expansion along path br continues to pressure p_r at the end of the piston stroke. The exhaust port is uncovered at point r , called the point of release. The cylinder pressure then drops to p_c (condenser pressure) as the steam rushes through the exhaust port. During the return stroke, represented by cd , the residual steam is removed from the cylinder. It is worth while to compare the diagram $abrcd$ with those which represent complete expansion for the same pressure range, as indicated by the dotted lines. If complete expansion to point c is to be achieved, early cutoff at b' is required, with resultant loss of power for the given cylinder size. On the other hand, complete expansion with cutoff at b would require increased cylinder size, as indicated by the location of c' . As usual, the work of the engine cycle is represented by the closed area on the p - v diagram, in this instance $abrcd$. Since ab and cd are constant-pressure processes and br is an adiabatic expansion, we have

$$\text{Work of the engine cycle} = A[p_a v_a + (e_r - e_r) - p_c v_c]$$

It will be observed that in this case the work is not equal to the difference between h_b and h_c . This results from the fact that, even for the assumptions made, the process from b to c is not reversible. Process rc is a highly irreversible throttling of the steam through the exhaust port.

The effect of this process is illustrated on the TS and hS diagrams shown in Figs. 8-21 and 8-22 respectively.

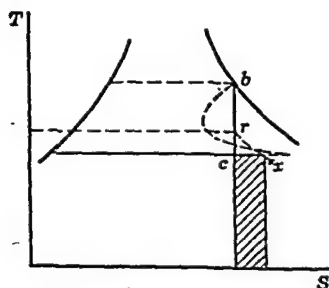


FIG. 8-21.

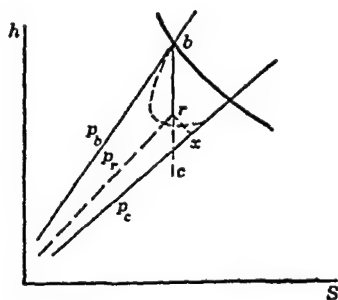


FIG. 8-22.

Whereas path bc represents reversible adiabatic expansion to condenser pressure p_c , path br represents adiabatic expansion to p_r , the pressure at point of release. The throttling change r to x , being irreversible, cannot be represented by a definite path, but results in an increase in entropy to point x . The shaded area on the TS diagram illustrates the resultant increase in unavailable energy.

Actually the cycle of an engine departs even further from path bc than is indicated above. This is the result of throttling on admission and of condensation and reevaporation while the steam is in the cylinder. As the steam enters the cylinder the cylinder wall and piston face are relatively cool compared to the temperature of the steam. Hence heat flows from the steam to the metal, with resulting condensation. As expansion proceeds and the steam temperature falls, heat flows from the metal to the steam and causes reevaporation. These are irreversible processes which cause an increase in entropy and hence a decrease in availability of energy. Probably the path of the changes is approximately represented by the dotted lines shown in Figs. 8-21 and 8-22. However, it must be recognized that the actual path of an irreversible process is not determinable. For further discussion of the influences which tend to reduce engine efficiency, together with the methods employed to minimize their effect, the student should refer to texts which treat the thermodynamics of steam engineering in detail.*

* W. N. Barnard, F. O. Ellenwood, and C. F. Hirshfeld, *Heat Power Engineering*, Wiley; P. J. Kiefer and M. C. Stuart, *Principles of Engineering Thermodynamics*, Wiley.

Engine Governing

One of the distinctly desirable features of the reciprocating steam engine is its flexibility, i.e., its ability to operate at practically constant speed under a variable load. This variation of power output at uniform speed is accomplished by changing the mean effective pressure either by throttling the admission steam or by varying the point of cutoff.

When throttling is used the steam supply is controlled by a throttle valve operated automatically by an engine governor. The engine speeds up as the load decreases and thereby causes the governor to move the throttle valve toward closure. The converse sequence occurs if the load is increased. Variation in the opening in the throttle valve changes both the pressure and the mass rate of flow of steam to the engine. Throttling is always a distinctly irreversible process and so is accompanied by an increase in entropy, with a consequent decrease in the availability of energy. This effect is somewhat offset by the reduction in initial condensation which results from the slight superheating of the steam incident to throttling.

The cutoff can also be advanced or delayed by means of a governor sensitive to the change in speed as the load varies. In this method of engine control the amount of steam admitted per cycle is varied but there is no change in its admission pressure. As the load decreases the point of cutoff is advanced (see Fig. 8-20) and more complete expansion occurs with a resultant decrease in the loss caused by irreversible throttling through the exhaust port. However this benefit may be largely nullified by the increase in initial condensation. Somewhat the converse effect may be presumed to occur when cutoff is delayed to provide for an increase in the power load. Under general conditions and for the usual range of engine loading greater efficiency results from governing by cutoff variation than by throttling.

Turbines

The turbine has an inherent advantage over the reciprocating steam engine in that it is a relatively light and compact unit capable of delivering high rotative speed.

The thermodynamic problem encountered in the ideal turbine is that of converting the available energy stored in boiler steam to kinetic energy. This is accomplished by increasing the velocity of the steam at the expense of its pressure. The problem of converting the kinetic energy of the fluid to shaft work is one of dynamics. In conformity with the particular dynamic principle employed in this conversion turbines are broadly classified as of the impulse or the reaction type. The ancients

knew the dynamic principles of impulse and reaction and applied them in simple devices employing expanding vapors. The same principles are utilized in the modern complex steam turbine which, since the latter part of the last century, has usurped the dominant position previously held by the reciprocating engine in commercial power development.

The essential mechanical elements of a turbine are:

1. A rotor attached to a revolving shaft through which it is desired to transmit work.
2. Suitably arranged blading or vanes attached to the rotor and upon which the dynamic effect of the high-velocity fluid is exerted.
3. A stationary casing, well sealed.
4. Stationary nozzles or blading attached to the casing which control the path and character of flow of the medium.

Both the design of blading and nozzles and the way in which the two are combined profoundly affect the character of the pressure and velocity changes of the fluid as it expands through the turbine.

The Expansion of Steam Through a Nozzle

This type of thermodynamic change was briefly presented in an example on page 33. In turbines the function of the nozzle is to increase velocity and produce a directed jet with a minimum loss of availability of energy through flow friction. The type of nozzle conventionally employed is *convergent-divergent* (see Fig. 2-4, page 33). Flow through a nozzle may be considered as adiabatic but is nevertheless irreversible because of the unavoidable fluid friction encountered. Since the energy transformed into heat by flow friction remains in the medium, the net effect is that the fluid emerges from the nozzle with a greater enthalpy than would be the case if expansion through the same pressure gradient occurred reversibly. Fig. 8-23 illustrates this effect. Path 1-2 represents reversible expansion, whereas at the end of irreversible expansion to the same condenser pressure, the medium is in state x . The effect is not without some benefit, however, for the

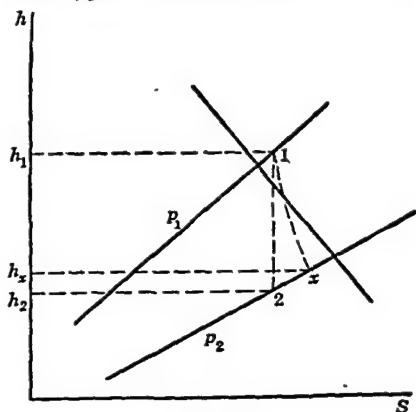


FIG. 8-23.

quality at state 1 is higher than that at state 2. This tendency to delay and reduce condensation is highly desirable in turbines.

Since the process of expansion is considered to be adiabatic and no external work is performed, for reversible flow the General Flow Equation reduces to

$$\frac{u_1^2}{2g} + Jh_1 = \frac{u_2^2}{2g} + Jh_2$$

and

$$u_2 = \sqrt{64.4 \times J(h_1 - h_2) + u_1^2}$$

The quantity u_1^2 may or may not be negligible, depending on the particular conditions. For the case where steam enters the nozzle from the steam line supply u_1^2 may be neglected and

$$u_2 = \sqrt{64.4 \times J(h_1 - h_2)}$$

When the irreversibility of the process is illustrated in Fig. 8-23 is taken into account

$$u_2 = \sqrt{64.4 \times J(h_1 - h_2) + u_1^2}$$

and if u_1 is negligible

$$u_2 = \sqrt{64.4 \times J(h_1 - h_2)}$$

Since h_2 is greater than h_2 it follows that the effect of the irreversible frictional process is to reduce the velocity of exit. The ratio $\frac{u}{u_2}$ is called the velocity coefficient (C_{vm}). Another coefficient of more interest to the engineer is the ratio

$$\frac{(u_2^2 - u_1^2)}{(u_2^2 - u_1^2)} = \frac{(h_1 - h_2)}{(h_1 - h_2)}$$

called nozzle efficiency. For negligible initial velocity

$$\text{velocity coefficient} = \sqrt{\text{nozzle efficiency}}$$

As yet no rational method has been devised for predicting nozzle efficiencies. Experiments have disclosed that efficiencies of actual steam turbine nozzles range from 0.90 to 0.97. They are subject to considerable fluctuation with the state of the steam flowing.*

The purpose of the following example is to give the student an appreciation of the magnitude of velocity which may be developed by expansion of steam through a nozzle.

Example

Steam initially at 200 lb per sq in. abs and 400° F expands through a nozzle to a discharge region at 150 lb per sq in. abs. C_{vm} for the nozzle is 0.98. Neglecting velocity of approach (u_1) determine the velocity of steam entering the discharge region.

* P. J. Laker and M. C. Stuart, *Principles of Engineering Thermodynamics*, Wiley.

Solution

$$u_x = 0.98 \sqrt{64.4 J(h_1 - h_2)}$$

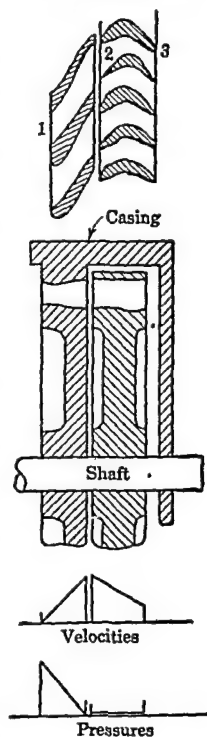
The steam is initially superheated. From the Mollier chart h_1 is 1209.8 Btu. Account has been taken of the irreversibility of the process by use of C_{vel} . Hence $h_2 = 1186$ Btu is determined as if the process were reversible and adiabatic.

$$\begin{aligned} \text{Then } u_x &= 0.98 \sqrt{64.4 \times 778(1209.8 - 1186)} \\ &= 1070 \text{ ft per sec} \end{aligned}$$

The Impulse Turbine

In this type of turbine the mechanical effect is derived mainly from the direct impact of the steam against the moving blades. Hence there is a transfer of momentum from fluid to blades by impulse, and the turbine is said to be of the impulse type. The work done on the moving blades as a result of this exchange of momentum is at the expense of the kinetic energy of the fluid. In order to produce the desired effect, the steam must strike the moving blades with a high relative velocity. Since the peripheral speed of the blades is also high, the steam must approach the blades with considerable absolute velocity. This velocity is attained from the expansion of the steam through stationary nozzles. Nicety of design is required in order that the steam shall strike the moving blades in the manner most effective for kinetic energy transfer with minimum shock loss and turbulence.*

The simplest type of impulse turbine consists of one element composed of a set of stationary nozzles and a single disk or rotor with blades set in the rim (see Fig. 8-24). A fundamental characteristic of the impulse turbine lies in the design of the blading which provides that the pressure at the exit of any row of moving blades shall be the same as the pressure at the entrance to that row of blades. There is also the theoretical objective that the enthalpy shall remain constant during the flow through the blade channel. If in fact the enthalpy were constant, the blade channel should be of constant cross-sectional area. However, because of turbulence and friction there is some increase in enthalpy with the resultant increase in entropy. There must therefore be a slight increase



Simple Impulse Turbine
FIG. 8-24.

(From G. J. Meyers, *Steam Turbines*, U. S. Naval Institute, p. 24.)

* G. J. Meyers, *Steam Turbines, A Treatise Covering U. S. Naval Practice*, United States Naval Institute, chap. 6.

in specific volume at point 3 over that at point 2 which must be provided for in the design of the blading

The flow equation across the blading for *reversible flow* reduces to

$$\frac{u_1^2}{2g} + Jh_1 = \frac{u_2^2}{2g} + Jh_2 + {}_1W'_2$$

Since theoretically $h_1 = h_2$

$${}_1W'_2 = \frac{u_1^2}{2g} - \frac{u_2^2}{2g} \text{ per lb of steam}$$

Actually at point 2 velocity is u_2 and enthalpy is h_2 as designated in the nozzle analysis on page 264. Call the actual enthalpy and velocity at point 3, h_3 and u_3 . Then

$$\frac{u_2^2}{2g} + Jh_2 = \frac{u_3^2}{2g} + Jh_3 + {}_2W'_3$$

For the nozzle

$$\frac{u_1^2}{2g} + Jh_1 = \frac{u_2^2}{2g} + Jh_2$$

By combining these two equations the work for the element is expressed by

$$W = J(h_1 - h_3) - \left(\frac{u_3^2}{2g} - \frac{u_1^2}{2g} \right) \text{ per lb of steam}$$

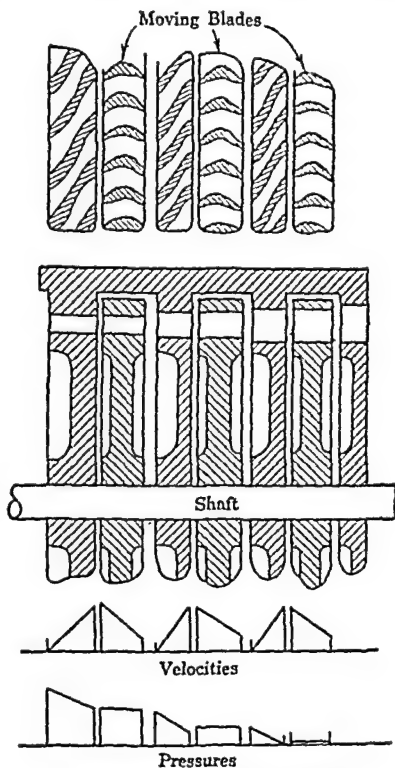
When u_1 is considered negligible this equation reduces to

$$W = J(h_1 - h_3) - \frac{u_3^2}{2g}$$

From this equation we conclude that aside from consideration of irreversibility which increases h_3 , increase in the work output requires a reduction in the absolute exit velocity u_3 . The reduction of u_3 to a minimum in one row of blading not only is difficult to achieve but involves excessively high rotor speed, especially if the initial pressure is high. In the early stages of turbine development many single-stage impulse turbines were built. But even with the boiler steam pressures of around 100 lb of that time, rotor speeds were so high as to cause trouble with centrifugal stresses, and reduction gears between the turbine and driven machinery were an essential part of the equipment. As development proceeded, pressure staging or velocity staging was employed to obtain complete expansion at suitable rotor speeds.

Pressure Staging — Impulse Turbine

In the simplest form the physical arrangement for pressure staging is that shown in Fig. 8-25. Each set of moving blades is in a separate compartment, and the steam passes from one compartment to another via the stationary expanding nozzles. Any number of such elements or stages may be used in series. Some commercial turbines have as many as 25 stages. By this arrangement the total pressure drop from steam to condenser is distributed over the series of elements and the jet velocity from any one set of nozzles is thereby reduced. Thus rotor speed is reduced and the leaving velocity is reduced to a minimum.



Impulse Turbine Pressure Staging

FIG. 8-25.

(From G. J. Meyers, *Steam Turbines*,
U. S. Naval Institute, p. 27.)

Velocity Staging — Impulse Turbine

Fig. 8-26 shows the general physical arrangement of a turbine employing velocity compounding. Multiple rows of moving blades in a single compartment are separated by rows of stationary blades. The latter serve to redirect the flow of the steam after its passage through a row of moving blades. The design of the stationary blading is such as to provide for *constant-pressure flow*, thus preserving the characteristic of the impulse turbine. Of course the steam velocity progressively decreases as kinetic energy is absorbed by each row of moving blades. No more than three or four velocity stages are used in any one pressure stage. However, velocity staging is usually repeated in successive compartments or pressure stages. This is called pressure-velocity compounding.

Reaction Turbines

In the conventional type of reaction turbine, force is exerted on the moving blades by a combination of impulse and reaction. The blades are set so that a part of the kinetic energy of the entering steam

is imparted to them by direct impact. Their form, however, is such that each of the channels between them has the effect of a nozzle. As the steam passes through the channel it expands to a lower pressure and produces a reactive force or recoil which assists in driving the blades. In a sense, the moving blades may be regarded as a row of moving nozzles. The reaction turbine is made up of alternate rows of moving and guide blades, as illustrated in Fig. 8-27. The guide blades, which

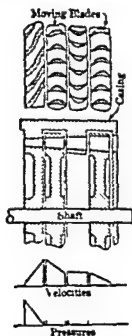


FIG. 8-26 Velocity Compounding Impulse Turbine. (From G. J. Meyers, *Steam Turbines*, U. S. Naval Institute, p. 29)

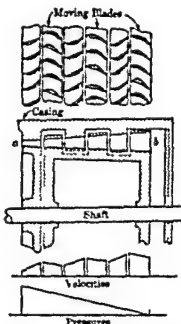


FIG. 8-27. Reaction Turbine (From G. J. Meyers, *Steam Turbines*, U. S. Naval Institute p. 35)

serve chiefly to direct the flow, are attached to the casing. The moving blades are attached to the rotor, which is in the form of a drum attached to the shaft. In a reaction turbine, the steam expands continuously from the supply line pressure to condenser pressure with gradually increasing velocity. If the rotor were held stationary and steam allowed to flow through the turbine, the blade passages taken together would constitute one long expansion nozzle (see *ab* in Fig. 8-27). In operation the steam first expands through a row of guide blades, acquires an initial velocity, and undergoes a drop in enthalpy. It then flows through the moving blades, does work on them, and at the same time expands to a lower

pressure. *A characteristic feature of the reaction turbine is the fact that there is a pressure drop from entrance to exit of any moving blade.* The blading of a reaction turbine is conventionally designed so that about the same amount of work is done by impulse as by reaction. The number of elements — that is, pairs of guide blades and moving blades — is a matter of design and may run as high as 40 or more.

The same expression for work is applicable to both impulse and reaction turbines.

$$W = J(h_a - h_b) - \left(\frac{u_b^2 - u_a^2}{2g} \right) \text{ per lb of steam}$$

In this equation a and b are the points of entrance and exit respectively of the flow stream. With actual values of enthalpy and absolute velocity substituted in the equation, account is taken of the loss caused both by irreversible flow and by the leaving velocity. If *both* admission and exit velocity for the turbine as a whole may be considered negligible and an assumption of adiabatic reversible flow is made, the equation above reduces to the familiar form

$$W = J(h_a - h_{b1})$$

Here h_{b1} is the value of enthalpy determined from the Mollier chart by following a constant-entropy line from the initial state point of the steam to its intersection with the pressure line corresponding to condenser pressure.

The reaction turbine may be readily designed to operate at low rotational speeds. It can also be operated at speeds different from those of the design with less efficiency loss than in the impulse turbine. Its disadvantage is that it is not well adapted for use with initial high-pressure steam because of unfavorable weight and space factors. Consequently large turbines made up wholly of reaction elements are now not much used. Modern practice tends toward either the impulse or the mixed turbine. The latter is a combination of the impulse and reaction types, with impulse stages at the high-pressure end followed by reaction blading after perhaps half of the total pressure drop has been achieved.

The following summary of types of turbines and the names associated with them is presented for reference purposes.

1. Simple impulse — DeLaval
2. Pressure staging impulse — Rateau
3. Velocity compounding impulse — Curtis
4. Pressure-velocity compounding impulse — Curtis
5. Reaction compounding — Parsons
6. Combined impulse and reaction (mixed) — Westinghouse, General Electric

PROBLEMS

- 1 Show by diagram a Rankine cycle on the AS and TS planes. Name the change of state representing each part of the cycle and the apparatus in which the change takes place. By using the values of enthalpy indicated on the Mollier chart determine the efficiency of the cycle. Tell how to find the external work done in a Rankine cycle.
- 2 The following cycle is approximately representative of a simple steam power plant, use a scale of $1 \text{ in} = 200^\circ \text{F}$ and $1 \text{ in} = 0.5$ entropy unit per lb of steam and plot the cycle on the TS diagram with origin at absolute zero. Feed water at $165 \text{ lb per sq in.}$ is warmed from 100°F to 366°F and then is completely vaporized. The steam then expands through a turbine to a pressure of $0.95 \text{ lb per sq in.}$, with an increase of entropy from 1.563 to 1.750 because of irreversibility. The steam is then condensed to water at $0.95 \text{ lb per sq in.}$, this is pumped into the boiler again as feed water. The compression of the water in the feed pump takes place adiabatically with a wholly negligible increase of temperature or entropy.

(a) Compute from your diagram the total amount of energy supplied in warming and vaporizing the water. (b) Check this value with the steam table. (c) Compute the minimum unavailable and maximum available portions of the total energy supply which might have been utilized if the cycle had been reversible, and from them determine the ideal maximum thermal efficiency if the cycle had been reversible. (d) From your diagram compute the energy actually discarded in the condenser, and check by analysis. Then determine the amount of energy that became unavailable because of the irreversibility. (e) Compute the energy that was actually available for delivery as work by the turbine, and determine the actual thermal efficiency of the cycle. (f) Make a scale diagram of the cycle on an AS chart (Mollier diagram), showing in dotted lines the same cycle with an ideal reversible expansion instead of the irreversible one.
- 3 A steam engine which exhausts to the atmosphere receives steam of 0.95 quality at $100 \text{ lb per sq in. abs pressure}$. The exhaust pressure is $15 \text{ lb per sq in. abs}$, and the steam consumption of the engine is $30 \text{ lb per indicated hp-hr}$. What is the thermal efficiency of the engine? What is the efficiency of the ideal Rankine cycle operating under the same conditions? What is the efficiency of the Carnot cycle operating between the same temperature limits?
- 4 Three plants are operated with a steam temperature of 750°F and the same vacuum in the condenser, but the first has an initial steam pressure of $1150 \text{ lb per sq in.}$ the second 550 , and the third 285 . Which plant is the most economical from the thermodynamic standpoint, if all operate with the same type of cycle?
- 5 One lb of steam at a pressure of $160 \text{ lb per sq in. abs}$ and quality 0.95 goes through an ideal Rankine cycle. The exhaust pressure is $15 \text{ lb per sq in. abs}$. Find (a) the work of the cycle, (b) the heat added to the cycle, (c) the efficiency of the cycle, (d) the steam consumption per horsepower hour.
- 6 One lb of steam at a pressure of $200 \text{ lb per sq in. abs}$ and 200°F superheat passes through a modified Rankine cycle. The release pressure is $15 \text{ lb per sq in. abs}$ and the exhaust pressure is $10 \text{ lb per sq in. abs}$. Calculate the net work and the efficiency of the cycle.

7. Two lb of steam at a pressure of 120 lb per sq in. abs and a volume of 8.154 cu ft perform an ideal Rankine cycle. The exhaust pressure is 3 lb per sq in. abs. (a) What is the efficiency of the cycle? (b) What is the net work of the cycle?
8. Steam is supplied to an engine at 150 lb gage and quality 0.98. The steam consumption is 18.6 lb per hp-hr. The absolute pressure in the condenser is 3.8 in. of mercury. (a) What is the enthalpy h supplied per horsepower hour? (b) What is the thermal efficiency? (c) If the engine expanded the steam adiabatically and reversibly, how many Btu would be available per 18.6 lb of steam? (d) What is the engine efficiency?

List of Symbols

- A* Area
- α Volume coefficient for real gases
- B* The gas constant in the equation $PV = MBT$ The units of *B* are ft lbs/lb/degree Rankine
- β Pressure coefficient for real gases
- Btu British thermal unit
- C* Molal specific heat (Also used to represent *chemical energy* in the general energy equation, to abbreviate centigrade, and as a general abbreviation for constant)
- c* Specific heat
- c_p Specific heat for a polytropic change
- c_p Specific heat for a constant pressure change
- c_v Specific heat for a constant volume change
- E* Intrinsic energy of *M* units of weight of a medium.
- e* Intrinsic energy of unit weight of a medium
- ΔE or Δe Change in intrinsic energy
- ξ emf of a cell
- F* Free energy (Also used to abbreviate Fahrenheit)
- ΔF Change in free energy
- g* Acceleration due to the attractive force of gravity exerted by the earth (Approximately 32.2 ft/sec² at the earth's surface)
- H* Enthalpy of *M* units of weight of a medium
- h* Enthalpy of unit weight of a medium
- ΔH or Δh Change in enthalpy
- i* Electric current
- J* Joule's equivalent of heat and work (778 ft lb equal 1 Btu, approximately)
- K* Used to abbreviate Kelvin
- k* The ratio c_p/c_v (Also used to represent other constant quantities in the equations of heat conduction the Newtonian law of attraction between masses, and Charles' Law)
- L* Latent heat
- M* Weight
- n* Number of mols in $PV = nRT$ (Also used to represent an undetermined constant exponent, e.g., $PV^n = \text{const}$)
- η Efficiency
- P* Total pressure
- p* Pressure force per unit area
- ρ Density
- Q* Heat quantity in transition to or from *M* units of weight of a medium.
- q* Heat quantity in transition to or from unit weight of a medium

- ΔQ or Δq . *Change in heat quantity.*
- ${}_1Q_2$. *Heat quantity added or withdrawn between state points 1 and 2 for M units of weight of a medium.*
- ${}_1q_2$. *Heat quantity added or withdrawn between state points 1 and 2 for unit weight of a medium.*
- R . *Universal gas constant. In $PV = nRT$, R has units of ft-lb/lb-mol/degree Rankine. (Also used as abbreviation for Rankine and to represent electrical resistance.)*
- r . *Compression ratio.*
- S . *Entropy of M units of weight of a medium.*
- s . *Entropy of unit weight of a medium.*
- ΔS or Δs . *Entropy change.*
- σ . *Radiation constant.*
- T . *Absolute temperature.*
- t . *Temperature, Fahrenheit or centigrade scales.*
- u . *Velocity.*
- V . *Volume of M units of weight of a medium.*
- v . *Volume of unit weight of a medium.*
- W . *Work.*
- ${}_1W_2$. *Work done between state points 1 and 2 for M units of weight of a medium.*
- ${}_1w_2$. *Work done between state points 1 and 2 for unit weight of a medium.*
- W_{\max} . *Maximum work.*
- ΔW_{\max} . *Change in the maximum work function.*
- x . *Quality of a vapor. The ratio of the weight of vapor present to the total weight of liquid and vapor present.*
- z . *Vertical distance above or below a given datum plane.*

TABLE I
DRY SATURATED STEAM: TEMPERATURE TABLE *

Temp. ° F	Atm Press., Lb Sq In.	Specific Volume				Enthalpy				Entropy				Temp. ° F
		Rel. Liquid v _f	Evap. v _{fg}	Rel. Vapor v _g	Rel. Vapor v _g	Rel. Liquid h _f	Evap. h _{fg}	Rel. Vapor h _g	Rel. Liquid s _f	Evap. s _{fg}	Rel. Vapor s _g			
28	0.04854	0.01602	33.04	33.04	0.00	1078.8	1078.8	0.0000	2.1877	2.1877	28	2.1877	2.1877	28
30	0.05094	0.01602	2947	2947	0.02	1074.3	1074.3	0.001	2.1706	2.1706	30	2.1706	2.1706	30
32	0.05334	0.01602	2644	2644	0.05	1071.3	1071.3	0.013	2.1535	2.1535	32	2.1535	2.1535	32
34	0.05574	0.01602	2346	2346	0.08	1068.3	1068.3	0.026	2.1364	2.1364	34	2.1364	2.1364	34
36	0.05814	0.01602	2048	2048	0.12	1065.3	1065.3	0.038	2.1193	2.1193	36	2.1193	2.1193	36
38	0.06054	0.01602	1750	1750	0.16	1062.3	1062.3	0.051	2.1022	2.1022	38	2.1022	2.1022	38
40	0.06294	0.01602	1452	1452	0.20	1059.3	1059.3	0.064	2.0851	2.0851	40	2.0851	2.0851	40
42	0.06534	0.01602	1154	1154	0.24	1056.3	1056.3	0.077	2.0680	2.0680	42	2.0680	2.0680	42
44	0.06774	0.01602	856	856	0.28	1053.3	1053.3	0.090	2.0509	2.0509	44	2.0509	2.0509	44
46	0.07014	0.01602	558	558	0.32	1050.3	1050.3	0.103	2.0338	2.0338	46	2.0338	2.0338	46
48	0.07254	0.01602	260	260	0.36	1047.3	1047.3	0.116	2.0167	2.0167	48	2.0167	2.0167	48
50	0.07494	0.01602	100	100	0.40	1044.3	1044.3	0.129	1.9996	1.9996	50	1.9996	1.9996	50
52	0.07734	0.01602	40	40	0.44	1041.3	1041.3	0.142	1.9825	1.9825	52	1.9825	1.9825	52
54	0.07974	0.01602	15	15	0.48	1038.3	1038.3	0.155	1.9654	1.9654	54	1.9654	1.9654	54
56	0.08214	0.01602	6	6	0.52	1035.3	1035.3	0.168	1.9483	1.9483	56	1.9483	1.9483	56
58	0.08454	0.01602	2	2	0.56	1032.3	1032.3	0.181	1.9312	1.9312	58	1.9312	1.9312	58
60	0.08694	0.01602	1	1	0.60	1029.3	1029.3	0.194	1.9141	1.9141	60	1.9141	1.9141	60
62	0.08934	0.01602	0.5	0.5	0.64	1026.3	1026.3	0.207	1.8970	1.8970	62	1.8970	1.8970	62
64	0.09174	0.01602	0.2	0.2	0.68	1023.3	1023.3	0.220	1.8799	1.8799	64	1.8799	1.8799	64
66	0.09414	0.01602	0.1	0.1	0.72	1020.3	1020.3	0.233	1.8628	1.8628	66	1.8628	1.8628	66
68	0.09654	0.01602	0.05	0.05	0.76	1017.3	1017.3	0.246	1.8457	1.8457	68	1.8457	1.8457	68
70	0.09894	0.01602	0.02	0.02	0.80	1014.3	1014.3	0.259	1.8286	1.8286	70	1.8286	1.8286	70
72	0.10134	0.01602	0.01	0.01	0.84	1011.3	1011.3	0.272	1.8115	1.8115	72	1.8115	1.8115	72
74	0.10374	0.01602	0.005	0.005	0.88	1008.3	1008.3	0.285	1.7944	1.7944	74	1.7944	1.7944	74
76	0.10614	0.01602	0.002	0.002	0.92	1005.3	1005.3	0.298	1.7773	1.7773	76	1.7773	1.7773	76
78	0.10854	0.01602	0.001	0.001	0.96	1002.3	1002.3	0.311	1.7602	1.7602	78	1.7602	1.7602	78
80	0.11094	0.01602	0.0005	0.0005	1.00	1000.0	1000.0	0.324	1.7431	1.7431	80	1.7431	1.7431	80
82	0.11334	0.01602	0.0002	0.0002	1.04	997.0	997.0	0.337	1.7260	1.7260	82	1.7260	1.7260	82
84	0.11574	0.01602	0.0001	0.0001	1.08	994.0	994.0	0.350	1.7089	1.7089	84	1.7089	1.7089	84
86	0.11814	0.01602	0.00005	0.00005	1.12	991.0	991.0	0.363	1.6918	1.6918	86	1.6918	1.6918	86
88	0.12054	0.01602	0.00002	0.00002	1.16	988.0	988.0	0.376	1.6747	1.6747	88	1.6747	1.6747	88
90	0.12294	0.01602	0.00001	0.00001	1.20	985.0	985.0	0.389	1.6576	1.6576	90	1.6576	1.6576	90
92	0.12534	0.01602	0.000005	0.000005	1.24	982.0	982.0	0.402	1.6405	1.6405	92	1.6405	1.6405	92
94	0.12774	0.01602	0.000002	0.000002	1.28	979.0	979.0	0.415	1.6234	1.6234	94	1.6234	1.6234	94
96	0.13014	0.01602	0.000001	0.000001	1.32	976.0	976.0	0.428	1.6063	1.6063	96	1.6063	1.6063	96
98	0.13254	0.01602	0.0000005	0.0000005	1.36	973.0	973.0	0.441	1.5892	1.5892	98	1.5892	1.5892	98
100	0.13494	0.01602	0.0000002	0.0000002	1.40	970.0	970.0	0.454	1.5721	1.5721	100	1.5721	1.5721	100

300	67.013	0.01745	6.449	6.406	269.59	910.1	1179.7	0.4359	1.1980	1.6350	390
310	77.68	0.01765	6.609	5.629	279.92	902.6	1182.5	0.4304	1.1727	1.6231	310
320	89.66	0.01765	4.896	4.914	290.28	894.0	1187.7	0.4037	1.1478	1.6115	320
330	103.06	0.01770	4.289	4.307	300.08	887.0	1187.7	0.4760	1.1233	1.6002	330
340	118.01	0.01787	3.770	3.788	311.13	879.0	1192.1	0.4900	1.0992	1.5891	340
350	134.63	0.01799	3.324	3.342	321.03	870.7	1192.3	0.5029	1.0754	1.5783	350
360	153.04	0.01811	2.930	2.947	332.18	862.2	1194.3	0.5158	1.0519	1.5677	360
370	173.37	0.01823	2.609	2.625	342.79	853.6	1196.3	0.5287	1.0287	1.5573	370
380	195.77	0.01836	2.317	2.335	353.45	844.6	1198.1	0.5413	1.0059	1.5471	380
390	220.37	0.01850	2.0691	2.0836	364.17	835.4	1199.5	0.5539	0.9832	1.5371	390
400	247.31	0.01864	1.8447	1.8633	374.97	826.0	1201.0	0.5664	0.9608	1.5272	400
410	276.75	0.01878	1.6312	1.6700	385.53	816.3	1202.1	0.5788	0.9386	1.5174	410
420	308.53	0.01894	1.4811	1.5600	396.77	806.3	1203.1	0.5912	0.9169	1.5078	420
430	343.72	0.01910	1.3308	1.4439	407.50	796.0	1203.8	0.6035	0.8947	1.4982	430
440	381.69	0.01926	1.1979	1.2471	418.50	785.4	1204.3	0.6158	0.8730	1.4887	440
450	422.6	0.0194	1.0799	1.0993	430.1	774.5	1204.6	0.6280	0.8513	1.4793	450
460	466.9	0.0195	0.9748	0.9944	441.4	763.2	1204.6	0.6402	0.8308	1.4700	460
470	514.7	0.0198	0.8811	0.9093	452.8	751.5	1204.3	0.6523	0.8083	1.4608	470
480	566.1	0.0200	0.7972	0.8173	464.4	739.4	1203.7	0.6645	0.7868	1.4513	480
490	621.4	0.0202	0.7221	0.7423	476.0	726.8	1202.8	0.6768	0.7653	1.4419	490
500	680.8	0.0204	0.6545	0.6740	487.8	713.9	1201.7	0.6887	0.7438	1.4325	500
510	742.4	0.0205	0.5935	0.5924	511.9	698.4	1198.2	0.7130	0.7006	1.4126	510
520	807.5	0.0215	0.4434	0.4640	536.6	686.0	1193.2	0.7374	0.6868	1.3942	520
530	876.1	0.0221	0.3647	0.3868	562.2	674.2	1189.4	0.7621	0.6721	1.3742	530
540	948.5	0.0228	0.2989	0.3217	588.9	661.4	1177.3	0.7872	0.6569	1.3532	540
550	1025.6	0.0235	0.2432	0.2608	617.0	648.5	1165.5	0.8131	0.6416	1.3307	550
560	1107.9	0.0247	0.1935	0.2201	646.7	636.0	1150.3	0.8398	0.6264	1.3082	560
570	1195.7	0.0260	0.1538	0.1798	676.6	624.0	1130.5	0.8673	0.6110	1.2857	570
580	1289.1	0.0278	0.1165	0.1442	714.2	611.2	1104.4	0.8987	0.5957	1.2632	580
590	1388.1	0.0305	0.0810	0.1115	757.3	598.9	1087.2	0.9351	0.5719	1.2407	590
600	1493.7	0.0369	0.0392	0.0761	823.3	586.1	1070.1	0.9905	0.5484	1.2182	600
700	3093.7	0.0503	0	0.0503	902.7	573.0	1052.7	1.0580	0	1.0580	700

* Abridged from "Thermodynamic Properties of Steam" by Joseph H. Keenan and Frederick G. Keyes. Copyright, 1937, by Joseph H. Keenan and Frederick G. Keyes.
G. Keyes.
Published by John Wiley & Sons, Inc., New York.

TABLE II

DRY SATURATED STEAM-PRINCIPAL TABLE

Abs Press. Lb Sq In.	Temp. ° F	Specific Volume			Enthalpy			Internal Energy			Abs Press. Lb Sq In.
		Rel. Liquid	Rel. Vapor	Sp	Rel. Liquid	Temp	Rel. Vapor	Rel. Liquid	Temp	Rel. Vapor	
14.694	213.00	0.01672	26.80	26.80	0.01672	213.00	0.01672	0.01672	213.00	0.01672	14.694
15	213.02	0.01672	26.80	26.80	0.01672	213.02	0.01672	0.01672	213.02	0.01672	15
16	213.04	0.01672	26.80	26.80	0.01672	213.04	0.01672	0.01672	213.04	0.01672	16
17	213.06	0.01672	26.80	26.80	0.01672	213.06	0.01672	0.01672	213.06	0.01672	17
18	213.08	0.01672	26.80	26.80	0.01672	213.08	0.01672	0.01672	213.08	0.01672	18
19	213.10	0.01672	26.80	26.80	0.01672	213.10	0.01672	0.01672	213.10	0.01672	19
20	213.12	0.01672	26.80	26.80	0.01672	213.12	0.01672	0.01672	213.12	0.01672	20
21	213.14	0.01672	26.80	26.80	0.01672	213.14	0.01672	0.01672	213.14	0.01672	21
22	213.16	0.01672	26.80	26.80	0.01672	213.16	0.01672	0.01672	213.16	0.01672	22
23	213.18	0.01672	26.80	26.80	0.01672	213.18	0.01672	0.01672	213.18	0.01672	23
24	213.20	0.01672	26.80	26.80	0.01672	213.20	0.01672	0.01672	213.20	0.01672	24
25	213.22	0.01672	26.80	26.80	0.01672	213.22	0.01672	0.01672	213.22	0.01672	25
26	213.24	0.01672	26.80	26.80	0.01672	213.24	0.01672	0.01672	213.24	0.01672	26
27	213.26	0.01672	26.80	26.80	0.01672	213.26	0.01672	0.01672	213.26	0.01672	27
28	213.28	0.01672	26.80	26.80	0.01672	213.28	0.01672	0.01672	213.28	0.01672	28
29	213.30	0.01672	26.80	26.80	0.01672	213.30	0.01672	0.01672	213.30	0.01672	29
30	213.32	0.01672	26.80	26.80	0.01672	213.32	0.01672	0.01672	213.32	0.01672	30
31	213.34	0.01672	26.80	26.80	0.01672	213.34	0.01672	0.01672	213.34	0.01672	31
32	213.36	0.01672	26.80	26.80	0.01672	213.36	0.01672	0.01672	213.36	0.01672	32
33	213.38	0.01672	26.80	26.80	0.01672	213.38	0.01672	0.01672	213.38	0.01672	33
34	213.40	0.01672	26.80	26.80	0.01672	213.40	0.01672	0.01672	213.40	0.01672	34
35	213.42	0.01672	26.80	26.80	0.01672	213.42	0.01672	0.01672	213.42	0.01672	35
36	213.44	0.01672	26.80	26.80	0.01672	213.44	0.01672	0.01672	213.44	0.01672	36
37	213.46	0.01672	26.80	26.80	0.01672	213.46	0.01672	0.01672	213.46	0.01672	37
38	213.48	0.01672	26.80	26.80	0.01672	213.48	0.01672	0.01672	213.48	0.01672	38
39	213.50	0.01672	26.80	26.80	0.01672	213.50	0.01672	0.01672	213.50	0.01672	39
40	213.52	0.01672	26.80	26.80	0.01672	213.52	0.01672	0.01672	213.52	0.01672	40
41	213.54	0.01672	26.80	26.80	0.01672	213.54	0.01672	0.01672	213.54	0.01672	41
42	213.56	0.01672	26.80	26.80	0.01672	213.56	0.01672	0.01672	213.56	0.01672	42
43	213.58	0.01672	26.80	26.80	0.01672	213.58	0.01672	0.01672	213.58	0.01672	43
44	213.60	0.01672	26.80	26.80	0.01672	213.60	0.01672	0.01672	213.60	0.01672	44
45	213.62	0.01672	26.80	26.80	0.01672	213.62	0.01672	0.01672	213.62	0.01672	45
46	213.64	0.01672	26.80	26.80	0.01672	213.64	0.01672	0.01672	213.64	0.01672	46
47	213.66	0.01672	26.80	26.80	0.01672	213.66	0.01672	0.01672	213.66	0.01672	47
48	213.68	0.01672	26.80	26.80	0.01672	213.68	0.01672	0.01672	213.68	0.01672	48
49	213.70	0.01672	26.80	26.80	0.01672	213.70	0.01672	0.01672	213.70	0.01672	49
50	213.72	0.01672	26.80	26.80	0.01672	213.72	0.01672	0.01672	213.72	0.01672	50
51	213.74	0.01672	26.80	26.80	0.01672	213.74	0.01672	0.01672	213.74	0.01672	51
52	213.76	0.01672	26.80	26.80	0.01672	213.76	0.01672	0.01672	213.76	0.01672	52
53	213.78	0.01672	26.80	26.80	0.01672	213.78	0.01672	0.01672	213.78	0.01672	53
54	213.80	0.01672	26.80	26.80	0.01672	213.80	0.01672	0.01672	213.80	0.01672	54
55	213.82	0.01672	26.80	26.80	0.01672	213.82	0.01672	0.01672	213.82	0.01672	55
56	213.84	0.01672	26.80	26.80	0.01672	213.84	0.01672	0.01672	213.84	0.01672	56
57	213.86	0.01672	26.80	26.80	0.01672	213.86	0.01672	0.01672	213.86	0.01672	57
58	213.88	0.01672	26.80	26.80	0.01672	213.88	0.01672	0.01672	213.88	0.01672	58
59	213.90	0.01672	26.80	26.80	0.01672	213.90	0.01672	0.01672	213.90	0.01672	59
60	213.92	0.01672	26.80	26.80	0.01672	213.92	0.01672	0.01672	213.92	0.01672	60
61	213.94	0.01672	26.80	26.80	0.01672	213.94	0.01672	0.01672	213.94	0.01672	61
62	213.96	0.01672	26.80	26.80	0.01672	213.96	0.01672	0.01672	213.96	0.01672	62
63	213.98	0.01672	26.80	26.80	0.01672	213.98	0.01672	0.01672	213.98	0.01672	63
64	214.00	0.01672	26.80	26.80	0.01672	214.00	0.01672	0.01672	214.00	0.01672	64
65	214.02	0.01672	26.80	26.80	0.01672	214.02	0.01672	0.01672	214.02	0.01672	65
66	214.04	0.01672	26.80	26.80	0.01672	214.04	0.01672	0.01672	214.04	0.01672	66
67	214.06	0.01672	26.80	26.80	0.01672	214.06	0.01672	0.01672	214.06	0.01672	67
68	214.08	0.01672	26.80	26.80	0.01672	214.08	0.01672	0.01672	214.08	0.01672	68
69	214.10	0.01672	26.80	26.80	0.01672	214.10	0.01672	0.01672	214.10	0.01672	69
70	214.12	0.01672	26.80	26.80	0.01672	214.12	0.01672	0.01672	214.12	0.01672	70
71	214.14	0.01672	26.80	26.80	0.01672	214.14	0.01672	0.01672	214.14	0.01672	71
72	214.16	0.01672	26.80	26.80	0.01672	214.16	0.01672	0.01672	214.16	0.01672	72
73	214.18	0.01672	26.80	26.80	0.01672	214.18	0.01672	0.01672	214.18	0.01672	73
74	214.20	0.01672	26.80	26.80	0.01672	214.20	0.01672	0.01672	214.20	0.01672	74
75	214.22	0.01672	26.80	26.80	0.01672	214.22	0.01672	0.01672	214.22	0.01672	75
76	214.24	0.01672	26.80	26.80	0.01672	214.24	0.01672	0.01672	214.24	0.01672	76
77	214.26	0.01672	26.80	26.80	0.01672	214.26	0.01672	0.01672	214.26	0.01672	77
78	214.28	0.01672	26.80	26.80	0.01672	214.28	0.01672	0.01672	214.28	0.01672	78
79	214.30	0.01672	26.80	26.80	0.01672	214.30	0.01672	0.01672	214.30	0.01672	79
80	214.32	0.01672	26.80	26.80	0.01672	214.32	0.01672	0.01672	214.32	0.01672	80
81	214.34	0.01672	26.80	26.80	0.01672	214.34	0.01672	0.01672	214.34	0.01672	81
82	214.36	0.01672	26.80	26.80	0.01672	214.36	0.01672	0.01672	214.36	0.01672	82
83	214.38	0.01672	26.80	26.80	0.01672	214.38	0.01672	0.01672	214.38	0.01672	83
84	214.40	0.01672	26.80	26.80	0.01672	214.40	0.01672	0.01672	214.40	0.01672	84
85	214.42	0.01672	26.80	26.80	0.01672	214.42	0.01672	0.01672	214.42	0.01672	85
86	214.44	0.01672	26.80	26.80	0.01672	214.44	0.01672	0.01672	214.44	0.01672	86
87	214.46	0.01672	26.80	26.80	0.01672	214.46	0.01672	0.01672	214.46	0.01672	87
88	214.48	0.01672	26.80	26.80	0.01672	214.48	0.01672	0.01672	214.48	0.01672	88
89	214.50	0.01672	26.80	26.80	0.01672	214.50	0.01672	0.01672	214.50	0.01672	89
90	214.52	0.01672	26.80	26.80	0.01672	214.52	0.01672	0.01672	214.52	0.01672	90
91	214.54	0.01672	26.80	26.80	0.01672	214.54	0.01672	0.01672	214.54	0.01672	91
92	214.56	0.01672	26.80	26.80	0.01672	214.56	0.01672	0.01672	214.56	0.01672	92
93	214.58	0.01672	26.80	26.80	0.01672	214.58	0.01672	0.01672	214.58	0.01672	93
94	214.60	0.01672	26.80	26.80	0.01672	214.60	0.01672	0.01672	214.60	0.01672	94
95	214.62	0.01672	26.80	26.80	0.01672	214.62	0.01672	0.01672	214.62	0.01672	95
96	214.64	0.01672	26.80	26.80	0.01672	214.64	0.01672	0.01672	214.64	0.01672	96
97	214.66	0.01672	26.80	26.80	0.01672	214.66	0.01672	0.01672	214.66	0.01672	97
98	214.68	0.01672	26.80	26.80	0.01672	214.68	0.01672	0.01672	214.68	0.01672	98
99	214.70	0.01672	26.80	26.80	0.01672	214.70	0.01672	0.01672	214.70	0.01672	99
100	214.72	0.01672	26.80	26.80	0.01672	214.72	0.01672	0.01672	214.72	0.01672	100

130	241.25	0.01760	3.728	312.44	877.0	1100.4	0.4016	1.0692	1.6878	312.05	1107.6	420
135	247.32	0.01766	3.455	318.31	872.0	1101.7	0.4095	1.0817	1.6812	318.38	1108.0	430
140	253.02	0.01762	3.220	324.82	868.2	1103.0	0.5000	1.0682	1.6761	324.36	1109.6	440
145	258.42	0.01815	3.015	330.51	863.0	1104.1	0.5138	1.0550	1.6694	330.61	1110.5	450
150	263.53	0.01815	2.834	336.03	859.2	1105.1	0.5204	1.0436	1.6600	336.39	1111.2	460
155	268.41	0.01822	2.675	341.00	854.0	1106.0	0.5206	1.0354	1.6500	340.52	1111.9	470
160	273.06	0.01827	2.532	346.03	850.8	1106.9	0.5325	1.0217	1.6342	346.42	1112.5	480
165	277.61	0.01833	2.404	350.70	846.8	1107.6	0.5391	1.0116	1.6197	350.15	1113.1	490
170	281.79	0.01839	2.288	355.36	843.0	1108.4	0.5435	1.0018	1.6043	354.68	1113.7	500
175	286.00	0.01848	2.184	360.00	838.1	1201.1	0.5675	1.0698	1.5253	375.14	1115.8	510
180	290.95	0.01865	2.075	364.84	833.0	1202.8	0.5879	0.9225	1.5104	382.79	1117.1	520
185	295.72	0.01913	1.920	369.09	828.2	1203.9	0.6050	0.8910	1.4906	408.46	1118.0	530
190	300.44	0.01931	1.783	373.20	823.0	1204.5	0.6214	0.8630	1.4844	422.6	1118.5	540
195	305.28	0.01950	1.654	377.24	817.4	1204.0	0.6356	0.8378	1.4794	435.5	1118.7	550
200	310.15	0.01970	1.532	381.24	811.0	1204.4	0.6487	0.8147	1.4654	447.6	1118.0	560
205	315.06	0.01990	1.416	385.19	804.0	1203.9	0.6608	0.7934	1.4542	458.8	1118.2	570
210	320.00	0.02010	1.304	389.09	797.0	1202.3	0.6720	0.7734	1.4454	469.4	1117.7	580
215	325.00	0.02030	1.196	392.94	790.0	1202.3	0.6828	0.7548	1.4374	479.4	1117.1	590
220	330.00	0.02050	1.092	396.74	783.0	1201.2	0.6928	0.7371	1.4293	488.8	1116.3	600
225	335.00	0.02070	0.992	400.50	775.0	1200.0	0.7019	0.7204	1.4223	508.0	1115.4	610
230	340.00	0.02090	0.897	404.24	767.0	1198.0	0.7108	0.7045	1.4162	526.0	1114.4	620
235	348.21	0.02100	0.809	407.94	759.0	1197.1	0.7194	0.6891	1.4095	542.0	1113.3	630
240	356.43	0.02110	0.726	411.60	750.0	1195.4	0.7275	0.6744	1.4028	557.0	1112.1	640
245	364.61	0.02120	0.646	415.24	741.0	1193.9	0.7356	0.6602	1.3957	570.0	1110.8	650
250	372.82	0.02130	0.569	418.84	732.0	1191.9	0.7430	0.6467	1.3897	588.4	1109.4	660
255	381.06	0.02140	0.496	422.40	723.0	1189.8	0.7505	0.6329	1.3840	605.1	1108.4	670
260	389.32	0.02150	0.426	425.92	714.0	1187.4	0.7575	0.6205	1.3780	622.2	1107.0	680
265	397.60	0.02160	0.358	429.40	705.0	1185.0	0.7640	0.6091	1.3720	639.7	1105.0	690
270	405.90	0.02170	0.292	432.84	696.0	1182.6	0.7693	0.5981	1.3659	657.7	1098.4	700
275	414.24	0.02180	0.228	436.24	687.0	1179.6	0.7743	0.5876	1.3594	676.2	1093.4	710
280	422.60	0.02190	0.166	439.60	678.0	1176.0	0.7790	0.5769	1.3529	695.1	1091.2	720
285	431.00	0.02200	0.106	442.92	669.0	1172.4	0.7833	0.5669	1.3461	714.2	1085.0	730
290	439.44	0.02210	0.048	446.20	660.0	1168.8	0.7875	0.5576	1.3397	733.6	1078.0	740
295	447.92	0.02220	0.000	449.44	651.0	1165.0	0.7915	0.5489	1.3329	753.2	1070.0	750
300	456.44	0.02230	0.000	452.64	642.0	1161.2	0.7953	0.5400	1.3261	773.0	1061.0	760
305	465.00	0.02240	0.000	455.80	633.0	1157.4	0.7990	0.5311	1.3197	792.8	1051.0	770
310	473.60	0.02250	0.000	458.92	624.0	1153.6	0.8026	0.5223	1.3131	812.6	1041.0	780
315	482.24	0.02260	0.000	462.00	615.0	1149.8	0.8061	0.5136	1.3067	832.4	1030.0	790
320	490.92	0.02270	0.000	465.04	606.0	1146.0	0.8095	0.5050	1.3007	852.2	1019.0	800
325	499.64	0.02280	0.000	468.12	597.0	1142.2	0.8128	0.4965	1.2947	872.0	1008.0	810
330	508.40	0.02290	0.000	471.24	588.0	1138.4	0.8160	0.4881	1.2887	891.8	997.0	820
335	517.20	0.02300	0.000	474.40	579.0	1134.6	0.8191	0.4798	1.2827	911.6	986.0	830
340	526.04	0.02310	0.000	477.60	570.0	1130.8	0.8221	0.4716	1.2767	931.4	975.0	840
345	534.92	0.02320	0.000	480.84	561.0	1127.0	0.8250	0.4634	1.2707	951.2	964.0	850
350	543.84	0.02330	0.000	484.12	552.0	1123.2	0.8278	0.4552	1.2647	971.0	953.0	860
355	552.80	0.02340	0.000	487.44	543.0	1119.4	0.8305	0.4470	1.2587	990.8	942.0	870
360	561.80	0.02350	0.000	490.80	534.0	1115.6	0.8332	0.4388	1.2527	1010.6	931.0	880
365	570.84	0.02360	0.000	494.16	525.0	1111.8	0.8358	0.4306	1.2467	1030.4	920.0	890
370	579.92	0.02370	0.000	497.52	516.0	1108.0	0.8383	0.4224	1.2407	1050.2	909.0	900
375	589.04	0.02380	0.000	500.88	507.0	1104.2	0.8408	0.4142	1.2347	1070.0	898.0	910
380	598.20	0.02390	0.000	504.24	498.0	1100.4	0.8432	0.4060	1.2287	1090.0	887.0	920
385	607.40	0.02400	0.000	507.60	489.0	1096.6	0.8456	0.3978	1.2227	1110.0	876.0	930
390	616.64	0.02410	0.000	510.96	480.0	1092.8	0.8479	0.3896	1.2167	1130.0	865.0	940
395	625.92	0.02420	0.000	514.32	471.0	1089.0	0.8502	0.3814	1.2107	1150.0	854.0	950
400	635.24	0.02430	0.000	517.68	462.0	1085.2	0.8525	0.3732	1.2047	1170.0	843.0	960
405	644.60	0.02440	0.000	521.04	453.0	1081.4	0.8548	0.3650	1.1987	1190.0	832.0	970
410	654.00	0.02450	0.000	524.40	444.0	1077.6	0.8570	0.3568	1.1927	1210.0	821.0	980
415	663.44	0.02460	0.000	527.76	435.0	1073.8	0.8592	0.3486	1.1867	1230.0	810.0	990
420	672.92	0.02470	0.000	531.12	426.0	1070.0	0.8614	0.3404	1.1807	1250.0	799.0	1000
425	682.40	0.02480	0.000	534.48	417.0	1066.2	0.8636	0.3322	1.1747	1270.0	788.0	1010
430	691.92	0.02490	0.000	537.84	408.0	1062.4	0.8658	0.3240	1.1687	1290.0	777.0	1020
435	701.48	0.02500	0.000	541.20	399.0	1058.6	0.8679	0.3158	1.1627	1310.0	766.0	1030
440	711.04	0.02510	0.000	544.56	390.0	1054.8	0.8700	0.3076	1.1567	1330.0	755.0	1040
445	720.64	0.02520	0.000	547.92	381.0	1051.0	0.8721	0.2994	1.1507	1350.0	744.0	1050
450	730.28	0.02530	0.000	551.28	372.0	1047.2	0.8742	0.2912	1.1447	1370.0	733.0	1060
455	739.96	0.02540	0.000	554.64	363.0	1043.4	0.8763	0.2830	1.1387	1390.0	722.0	1070
460	749.68	0.02550	0.000	558.00	354.0	1039.6	0.8784	0.2748	1.1327	1410.0	711.0	1080
465	759.44	0.02560	0.000	561.36	345.0	1035.8	0.8805	0.2666	1.1267	1430.0	700.0	1090
470	769.24	0.02570	0.000	564.72	336.0	1032.0	0.8826	0.2584	1.1207	1450.0	689.0	1100
475	779.08	0.02580	0.000	568.08	327.0	1028.2	0.8847	0.2502	1.1147	1470.0	678.0	1110
480	788.96	0.02590	0.000	571.44	318.0	1024.4	0.8868	0.2420	1.1087	1490.0	667.0	1120
485	798.88	0.02600	0.000	574.80	309.0	1020.6	0.8889	0.2338	1.1027	1510.0	656.0	1130
490	808.84	0.02610	0.000	578.16	300.0	1016.8	0.8910	0.2256	1.0967	1530.0	645.0	1140
495	818.84	0.02620	0.000	581.52	291.0	1013.0	0.8931	0.2174	1.0907	1550.0	634.0	1150
500	828.88	0.02630	0.000	584.88	282.0	1009.2	0.8952	0.2092	1.0847	1570.0	623.0	1160
505	838.96	0.02640	0.000	588.24	273.0	1005.4	0.8973	0.2010	1.0787	1590.0	612.0	1170
510	849.08	0.02650	0.000	591.60	264.0	1001.6	0.8994	0.1928	1.0727	1610.0	601.0	1180
515	859.24	0.02660	0.000	594.96	255.0	997.8	0.9015	0.1846	1.0667	1630.0	590.0	1190
520	869.44	0.02670	0.000	598.32	246.0	994.0	0.9036	0.1764	1.0607	1650.0	579.0	1200
525	879.68	0.02680	0.000	601.68	237.0	990.2	0.9057	0.1682	1.0547	1670.0	568.0	1210
530	889.96	0.02690	0.000	605.04	228.0	986.4	0.9078	0.1600	1.0487	1690.0	557.0	1220
535	899.28	0.02700	0.000	608.40	219.0	982.6	0.9099	0.1518	1.0427	1710.0	546.0	1230
540	909.64	0.02710	0.000	611.76	210.0	978.8	0.9120	0.1436	1.0367	1730.0	535.0	1240
545	919.96	0.02720	0.000	615.12	201.0	975.0	0.9141	0.1354	1.0307	1750.0	524.0	1250
550	930.32	0.02730	0.000	618.48	192.0	971.2	0.9162	0.1272	1.0247	1770.0	513.0	1260
555	940.72	0.02740	0.000	621.84	183.0	967.4	0.9183	0.1190	1.0187	1790.0	502.0	1270
560	951.16	0.02750	0.000	625.20	174.0	963.6	0.9204	0.1108	1.0127	1810.0	491.0	1280
565	961.64	0.02760	0.000	628.56	165.0</							

TABLE III
PROPERTIES OF SUPERHEATED STEAM *

Abs Press., lb per sq in. (Sat. Temp.)	Temperature—Degrees Fahrenheit											
	300	400	500	600	700	800	900	1000	1100	1200	1300	1400
397.6	4.2	812.0	871.6	931.2	990.8	1050.4	1109.9	1169.5	1229.1	1288.7	1348.3	1407.8
397.6	1194.6	1248.2	1301.8	1355.4	1409.0	1462.6	1516.2	1569.8	1623.4	1677.0	1730.6	1784.2
397.6	2.0413	2.1170	2.2233	2.3702	2.5612	2.8022	3.0932	3.4342	3.8252	4.2662	4.7572	5.2982
397.6	102.78	102.78	114.22	126.66	139.10	151.54	163.98	176.42	188.86	201.30	213.74	226.18
397.6	114.48	114.48	126.92	139.36	151.80	164.24	176.68	189.12	201.56	214.00	226.44	238.88
397.6	1.8118	1.8370	1.9913	2.0977	2.2520	2.4063	2.5606	2.7149	2.8692	3.0235	3.1778	3.3321
397.6	38.85	48.00	57.05	66.10	75.15	84.20	93.25	102.30	111.35	120.40	129.45	138.50
397.6	114.48	114.48	126.92	139.36	151.80	164.24	176.68	189.12	201.56	214.00	226.44	238.88
397.6	1.7527	1.8172	1.9172	2.0463	2.2063	2.3913	2.6023	2.8393	3.1023	3.3913	3.7063	4.0473
397.6	30.23	34.08	38.78	43.48	48.18	52.88	57.58	62.28	66.98	71.68	76.38	81.08
397.6	1192.6	1219.0	1245.4	1271.8	1298.2	1324.6	1351.0	1377.4	1403.8	1430.2	1456.6	1483.0
397.6	1.8100	1.8745	1.9745	2.1036	2.2636	2.4486	2.6596	2.8966	3.1596	3.4486	3.7636	4.1046
397.6	25.43	28.43	31.43	34.43	37.43	40.43	43.43	46.43	49.43	52.43	55.43	58.43
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.7806	1.8451	1.9451	2.0742	2.2342	2.4192	2.6302	2.8672	3.1302	3.4192	3.7342	4.0752
397.6	21.040	23.040	25.040	27.040	29.040	31.040	33.040	35.040	37.040	39.040	41.040	43.040
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.7994	1.8639	1.9639	2.0930	2.2530	2.4380	2.6490	2.8860	3.1490	3.4380	3.7530	4.0940
397.6	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259	15.259	16.259	17.259	18.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376.4	1402.8	1429.2	1455.6	1482.0
397.6	1.6472	1.7117	1.8117	1.9408	2.0998	2.2898	2.5108	2.7638	3.0488	3.3638	3.7088	4.0838
397.6	3.259	4.259	5.259	6.259	7.259	8.259	9.259	10.259	11.259	12.259	13.259	14.259
397.6	1191.6	1218.0	1244.4	1270.8	1297.2	1323.6	1350.0	1376				

140 (363.02)	3.954 1276.2 1.6083	4.413 1326.4 1.7190	4.801 1376.8 1.7848	5.301 1427.3 1.8603	5.738 1478.2 1.8451	6.172 1528.7 1.8817	6.604 1581.9 1.9163	7.038 1634.9 1.9493	7.805 1745.5 2.0110	8.782 1856.7 2.0683
160 (363.63)	3.008 1217.0 1.5908	3.443 1273.1 1.6810	3.849 1328.0 1.7491	4.244 1378.7 1.7911	4.631 1428.4 1.8301	5.015 1477.0 1.8607	5.390 1526.7 1.8867	5.775 1575.4 1.9044	6.152 1624.5 1.9212	6.908 1743.2 1.9962
180 (373.06)	2.649 1214.0 1.5745	3.044 1271.0 1.6373	3.411 1323.5 1.6894	3.764 1374.7 1.7355	4.110 1425.6 1.7776	4.452 1476.8 1.8167	4.792 1528.0 1.8534	5.129 1579.1 1.8882	5.466 1630.1 1.9212	6.804 1742.9 1.9831
200 (381.79)	2.301 1210.3 1.5594	2.726 1268.0 1.6340	3.080 1322.1 1.6767	3.380 1373.6 1.7232	3.693 1424.8 1.7655	4.002 1476.2 1.8048	4.309 1528.0 1.8415	4.613 1579.6 1.8763	4.917 1631.7 1.9094	6.123 1743.6 1.9713
220 (389.86)	2.125 1206.6 1.5463	2.465 1266.7 1.6117	2.772 1320.7 1.6652	3.090 1372.0 1.7120	3.352 1423.0 1.7545	3.634 1475.5 1.7939	3.913 1527.5 1.8308	4.191 1579.6 1.8666	4.467 1632.3 1.8987	5.565 1742.3 1.9607
240 (397.37)	1.9276 1202.6 1.5319	2.247 1264.5 1.6003	2.533 1319.2 1.6540	2.804 1371.5 1.7017	3.068 1423.2 1.7444	3.327 1474.8 1.7839	3.584 1526.9 1.8209	3.839 1579.6 1.8568	4.093 1632.0 1.8880	5.100 1742.0 1.9510
260 (404.42)	1.7623 1198.7 1.5187	2.063 1262.3 1.5897	2.330 1317.7 1.6447	2.582 1370.4 1.6922	2.827 1422.3 1.7352	3.067 1474.2 1.7748	3.305 1526.3 1.8118	3.541 1579.1 1.8467	3.776 1632.5 1.8799	4.707 1741.7 1.9420
280 (411.05)	1.6047 1194.0 1.5066	1.9047 1260.0 1.5796	2.156 1315.2 1.6354	2.392 1369.4 1.6834	2.621 1421.5 1.7265	2.845 1473.5 1.7662	3.066 1525.8 1.8033	3.288 1578.6 1.8383	3.504 1632.1 1.8716	4.370 1741.4 1.9337
300 (417.33)	1.4675 1190.0 1.4941	1.7675 1257.6 1.5701	2.005 1314.7 1.6268	2.227 1368.3 1.6751	2.442 1420.6 1.7184	2.652 1472.8 1.7582	2.859 1525.2 1.7954	3.065 1578.1 1.8305	3.269 1631.7 1.8638	4.078 1741.0 1.9260
350 (431.72)	1.4923 1251.6 1.5481	1.7036 1310.9 1.6070	1.9800 1365.5 1.6563	2.084 1418.5 1.7002	2.266 1471.1 1.7403	2.445 1523.8 1.7777	2.622 1577.0 1.8130	2.798 1630.7 1.8463	2.968 1740.3 1.8986	3.403 1853.1 1.9663
400 (444.60)	1.2851 1245.1 1.5281	1.4770 1308.9 1.5894	1.6508 1362.7 1.6398	1.8161 1416.4 1.6842	1.9767 1469.4 1.7247	2.134 1522.4 1.7623	2.290 1575.8 1.7977	2.445 1629.6 1.8311	2.751 1739.5 1.8936	3.055 1852.5 1.9513

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G. Keyes.
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1400 (587.10)	\bar{v} h..... g.....	0.3174 1193.0 1.3030	0.3300 1218.4 1.3877	0.2580 1240.4 1.4070	0.3753 1260.3 1.4258	0.3012 1278.5 1.4419	0.4002 1295.5 1.4607	0.4714 1309.1 1.5177	0.5281 1433.1 1.5600	0.5805 1493.2 1.6003	0.6780 1521.7 1.6830	0.7757 1571.7 1.7489	0.8040 1600.0 1.8083
1600 (604.90)	\bar{v} h..... g..... 1187.8	0.2733 1187.8 1.3489	0.2936 1215.2 1.3741	0.3112 1238.7 1.3962	0.3271 1259.6 1.4137	0.3417 1278.7 1.4303	0.4034 1308.4 1.4904	0.4553 1425.3 1.5476	0.5027 1487.0 1.5914	0.5906 1504.6 1.6669	0.6738 1570.5 1.7228	0.7545 1637.5 1.7920
1800 (621.03)	\bar{v} h..... g..... 1185.1	0.2407 1185.1	0.2597 1214.0 1.3377	0.2897 1238.5 1.3638	0.2780 1258.5 1.3856	0.2907 1278.5 1.4044	0.3502 1347.2 1.4705	0.3980 1417.4 1.5301	0.4421 1480.8 1.5752	0.5218 1600.4 1.6520	0.5998 1717.3 1.7185	0.6993 1835.0 1.7780
2000 (638.82)	\bar{v} h..... g..... 1145.6	0.1936 1145.6 1.2945	0.2101 1184.0 1.3300	0.2337 1214.8 1.3504	0.2480 1236.5 1.3783	0.2680 1258.5 1.4044	0.3074 1347.2 1.4570	0.3532 1409.2 1.5139	0.3935 1474.5 1.5603	0.4608 1590.1 1.6384	0.5353 1714.1 1.7055	0.6011 1832.5 1.7660
2800 (668.13)	\bar{v} h..... g.....	0.1484 1132.3 1.2087	0.1680 1176.8 1.3073	0.2204 1303.6 1.4127	0.2710 1367.8 1.4772	0.3001 1458.3 1.5273	0.3078 1585.3 1.6088	0.4244 1705.1 1.6775	0.4764 1820.2 1.7380
3000 (695.36)	\bar{v} h..... g.....	0.0984 1080.7 1.1900	0.1760 1207.2 1.3690	0.2159 1365.5 1.4439	0.2470 1441.8 1.4984	0.3018 1574.3 1.5837	0.3505 1698.0 1.6540	0.3906 1819.9 1.7163
3206.2 (705.40)	\bar{v} h..... g.....	0.1583 1250.5 1.3508	0.1981 1355.2 1.4309	0.2288 1434.7 1.4874	0.2806 1509.8 1.5742	0.3267 1604.6 1.6452	0.3703 1813.0 1.7080
3800	\bar{v} h..... g.....	0.0306 780.5 0.0515	0.1364 1224.9 1.3241	0.1702 1340.7 1.4127	0.2058 1424.5 1.4723	0.2540 1503.3 1.5615	0.2977 1689.8 1.6330	0.3381 1813.0 1.6905
4000	\bar{v} h..... g.....	0.0287 763.8 0.0347	0.1052 1174.8 1.2767	0.1402 1314.4 1.3827	0.1743 1406.8 1.4482	0.2102 1552.1 1.5417	0.2481 1681.7 1.6154	0.2843 1807.3 1.6705
4800	\bar{v} h..... g.....	0.0270 753.6 0.0235	0.0708 1113.9 1.2204	0.1226 1288.5 1.3529	0.1600 1398.4 1.4263	0.1917 1540.8 1.5235	0.2273 1673.5 1.5990	0.2603 1800.9 1.6640
5000	\bar{v} h..... g.....	0.0268 740.4 0.0162	0.0593 1047.1 1.1622	0.1036 1266.5 1.3231	0.1303 1369.5 1.4034	0.1608 1529.5 1.5006	0.2027 1704.3 1.5830	0.2329 1813.0 1.6409
5500	\bar{v} h..... g.....	0.0262 741.3 0.0090	0.0403 986.0 1.1093	0.0880 1224.1 1.2930	0.1143 1340.3 1.3821	0.1510 1518.2 1.4908	0.1925 1657.0 1.5699	0.2100 1788.1 1.6369

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Index

- Absolute pressure, 11
 gage, 11
 Absolute temperature, 13
 thermodynamic scale of, 62
 Absolute zero, 12, 13
 Adiabatic change, 38
 irreversible, 75
 reversible non-flow, 84
 Adiabatic change of state, of perfect gas,
 146; entropy change for, 150; evalua-
 tion of ${}_1Q_2$, ${}_1W_2$, and ΔE for, 149
 of vapors, 186
 Air, compressed, 200
 engine, 214
 free, 210, 211
 Air compression, 200
 air engine, 214
 clearance, 210
 clearance factor, 213
 clearance ratio, 212
 clearance volume, 211
 free air, 210
 reheating, 215
 volumetric efficiency, 210
 Air compression cycle, 201
 effect of water jacketing, 207
 evaluation of work of, 204
 multi-stage compression, 209
 overall efficiency, 216
 source of work done by, 205
 Air standard efficiency, 225
 Diesel cycle, 231
 internal combustion engines, 225
 Otto cycle, 226
 Andrews, 117
 Atmosphere, international, 162
 Atmospheric pressure, 11
 Availability of heat energy, 53
 Available heat, 77
 Avogadro's Law, 112, 126

 B (gas constant), dimensions of, 112
 Baker, John B., 235
 Beattie-Bridgeman characteristic equation
 for gases, 117
 Beau de Rochas, 219
 Bernoulli Equation, 25, 27
 Binary cycle, 252, 255
 Black, James, 14

 Boiler pressure, effect on efficiency of Rankine
 Cycle, 249
 Boyle, Robert, 105
 Boyle's Law, 105
 Brake dynamometer, 224
 Brake power, I. C. engine, 223, 224
 Brayton, George B., 219
 Btu (British thermal unit) defined, 14

 c_n (specific heat polytropic change), 43
 evaluation for perfect gas, 154
 c_p (specific heat constant-pressure change),
 15
 relation to c_v , 122
 variable, 120
 c_v (specific heat constant-volume change),
 15
 relation to c_p , 122
 variable, 120
 C_{vel} (velocity coefficient), 264
 Callendar's characteristic equation for steam,
 117
 Caloric theory of heat, 14
 Caloric defined, 14
 Calorimeter, barrel, 195
 separating, 195
 throttling, 193; limitations, 194
 Cards, indicator, 49
 Carnot, Sadi, 4, 55
 Carnot cycle, 55
 description of operation, 55
 diagram, 58, 72; TS plane, 77
 efficiency, 59, 63; factors affecting, 64
 illustrative examples, 64
 Rankine cycle comparison, 241
 Carnot principle, 59, 62
 Celsius, 8
 Centigrade temperature scale, 13
 Change of state, gaseous, 105, 135
 of perfect gas, adiabatic, 146; constant
 pressure, 140; constant volume, 135;
 isometric, 135; isothermal, 143; poly-
 tropic, 150
 of vapors, 161
 water vapor, 177; adiabatic, 186; constant
 enthalpy, 190; constant pressure, 180;
 constant volume, 178; isothermal, 182;
 polytropic, 187

- Changes, thermodynamic, limiting types of, 37
- adiabatic, 38
 - isometric, 38
 - isopiestic, 38
 - isothermal, 37
 - polytropic, 38
- Characteristic equation, 9
- of perfect gas, 108
- Characteristic equations, 114, 117
- Beattie Bridgeman, 117
 - Callendar, 117
 - Clausius, 117
 - Dieterich, 117
 - Lee's, 117
 - of vapors, 116
 - van der Waals', 114
- Charles, Jacques, 12, 106
- Charles' Law, 12, 106
- Clapeyron equation, 163
- derivation, 164-166
- Claude, Georges, 4
- Clausius, 4, 65, 166
- characteristic equation for perfect gases, 117
- Clausius-Clapeyron equation, 166
- Clearance, air compressor, 210
- Clearance factor, air compression, 213
- Clearance ratio, air compression, 212
- Clearance volume, air compression, 211
- Coefficients, Joule-Thompson, 132
- pressure (β), 110
 - velocity (nozzle), C_{vd} , 264
 - volume (α), 110
- Composition, volume, for gases, 126
- weight, for gases, 126
- Compressed air, 200
- Compressed air cycle, 201
- effect of water jacketing, 207
 - engine, 214
 - evaluation of work of, 204
 - multi-stage compression, 209
 - overall efficiency, 216
 - source of work done by, 205
- Compressibility factors, 119
- Compression ratio, 221
- Compressor, air, capacity, 210
- clearance, 210
 - evaluation of work of, 203, 204
 - volumetric efficiency, 210
- Condenser, steam plant use, 240
- Condenser temperature, effect of change in Rankine cycle, 246
- Conduction of heat, 29
- Conservation of Energy, Law of, 19, 25
- Constant-pressure change, non flow, 85
- of perfect gas, 140, entropy change, 143, evaluation of ${}_1Q_2$, ${}_1H_2$, ΔE , 140
 - of water vapor, 180
- Constant pressure process, 38
- Constant temperature change, 37
- See also* Isothermal change
- Constant volume change, of perfect gas, entropy change, 139, evaluation of ${}_1Q_2$, 138, work of, 136
- of water vapor, 178
- Constant-volume process, 38
- Constants, for van der Waals' equation, 115
- $A = a_p/c_v$, 137
 - R and B , for gas, 112
 - universal gas, 115, 115
- Continuity, equation of, 27
- Convection, 21
- Coordinates, thermodynamic, 8
- enthalpy, 31
 - entropy, 71
 - functional relation of P , V , and T , 9
 - pressure, 9
 - temperature, 9
 - volume, 9
- Critical point, 118
- Critical pressure, 117, 118
- Critical properties, table, 118
- Critical temperature, 117, 118
- Critical volume, 117, 118
- Cutoff, point of, 260
- Cycle, Carnot, 55
- irreversible, 74
 - reversible, 74
 - thermodynamic, 42
- Cycles, air compression, 201
- internal combustion engine, 219, Duesl, 218, 220, 221, Lenoir, 219, Otto, 218, 219, 220, 221
 - steam, 239
 - binary, 252, 255, Ideal Rankine, 241, incomplete expansion, 257, regenerative feed heating, 252, reheating, 252, 254, reheating-regenerative, 254
- Cyclical process, 42
- work done in, 48
- Dalton, 13
- Davy, Sir Humphry, 3
- Degradation of energy, 67
- Diesel, Rudolph, 220
- Diesel cycle, 218, 220, 221
- air-standard efficiency, 231
 - diagram of ideal 4-stroke cycle, 230
- Dieterich, characteristic equation for gases, 117
- Differential, exact, 40
- E , e (intrinsic energy), 23
- Eastman, E. D., 121
- Eastman's equations for variable specific heat, 120
- Efficiency, Carnot, 59, 63, factors affecting, 64

- Efficiency (*cont.*)
 internal combustion engines, air standard analysis, 225; Diesel cycle, 231; indicated thermal, 224; mechanical, 224; methods of computing, 222; Otto cycle, 226; overall thermal, 224
 Rankine cycle, methods of improving, 246; thermal, 243
 turbine nozzle, 264
 volumetric, for air compressor, 210
- Energy, availability of heat, 53
 conservation of, law, 19, 25
 degradation of, 67
 free, 86, 88
 heat, 20
 intrinsic, 23, 24
 transformation, 19, 20
 unavailable, 80
- Energy equation, Bernoulli, 25, 27
 general, 26
 non-flow, 57
- Engine, air, 214
- Engines, internal combustion, 218; Brayton, 219, 220; Diesel, 220, 221; four-stroke cycle, 221; Lenoir, 219; multiple cylinder, 221; Otto, 219; two-stroke cycle, 221
 steam, 239; complete expansion, 258; governing, 262; incomplete expansion, 259; non-expansion, 258; reciprocating, 257; turbine, 239
- Enthalpy (h), 31
 a point function, 93
 and heat of chemical reaction, 85, 91, 94
 application, 33, 36, 85
 change of, for evaporation, 174; for superheating, 174
 of wet vapor, 170
- Entropy, 67
 a point function, 71, 74, 76
 a thermodynamic coordinate, 76
 algebraic sign of, 76
 an extensive factor of heat, 68, 69
 and irreversibility, 77
 and unavailable heat, 79
 change, 69, 70; for superheated vapor, 172; for wet vapor, 170; of a system, 73; of closed cycle, 73; of irreversible process, 79; of perfect gas for various changes of state, 139, 143, 146, 150, 156
 defined, 68
 properties of, 76
 use of, 77
- Equation, Bernoulli, 25, 27
 general energy, 26
 Gibbs-Helmholtz, 93, 95
- Equations, characteristic for gases, 114, 117
 characteristic for vapors, 161; Clapeyron, 163; Clausius-Clapeyron, 166; Keenan and Keys, 162
- Equations (*cont.*)
 of perfect gas law, empirical adaptation, 119
 variable specific heat, Eastman's, 120
- Ericsson, John, 218
- Eugen, 99
- Evaporation, enthalpy change of, 174
 latent heat of, 165, 174
 pressures of, 163-167
 temperatures of, 163-167
- Evaporation process, 162
- Exact differential, 40
- Exponent " n ," 39, 45, 106
- F (free energy), 86, 88
 relation to W_{\max} , 89
- Factors, compressibility, 119
- Fahrenheit temperature scale, 13
- First Law of Thermodynamics, 3, 4, 19, 25
- Free air, 210, 211
- Free energy, 86, 88
- Free energy change, equation, 95
- Free expansion, 131
- Frictionless processes, 53, 54
- Functions, F (free energy), 86, 88
 point and path, 39
 W_{\max} (maximum work), 86
- Gage pressure, 11
- Gages, pressure, 11
 absolute scale, 11
 conventional, 11
 vacuum, 11
- Gas, perfect, 106, 108; characteristic equation of, 108
- Gas constant, 112
 R and B , 112
 universal, 113, 115
- Gas law, ideal, 107, 109
 application, 113
- Gas thermometer, 110
- Gaseous change of state, 105, 135
- Gaseous mixtures, 126
 apparent molecular weight for, 127
 gas constant for, 127
 specific heat of, 127, 128
- Gases, Linde process for liquefaction of, 133
 permanent, 105
 thermodynamic properties of, 105
 variable specific heat, 120
 volume, 126
 weight composition of, 126
- Gay-Lussac, 13, 106, 129
- Gay-Lussac's Law, 106
- General energy equation, 26
 of thermodynamics, 28, 30
- General flow equation for turbine nozzles, 264
- Gerry, H. T., 162

- Gibbs, Willard, 89
 Gibbs-Helmholtz equation, 93, 95
 Goodenough, George A., 235
 Governing, steam engine, 262
- H* (enthalpy), 32
 heat of chemical reaction, 85, 91, 94
- Heat, and work, 19
 available, 77
 conduction, 20
 convection, 21
 defined, 20
 energy in transition, 20, 21
 evaluation of Q , 42
 infinite source, 56
 latent, 170, of evaporation, 165
 mechanical equivalent of, 22
 radiation, 21
 representation by an area, 75
 specific, 14, 15, variable for gases, 120
 unavailable, 77
 units of, 14
- Heat energy availability of, 53
 Heat of reaction, 91, 94
 and maximum work, 91
 equation for, 95
- Horsepower, indicated, 223
 Hotwell pump, 246
 Hotwell tank, 240
- Ideal gas, 107
 changes of state, 135, 140
 Ideal gas law, 107, 109
 application, 113
- Impulse turbine, 265
 pressure staging, 267
 velocity staging, 267
- Indicated horsepower of I. C. engine, 223
 Indicated thermal efficiency of I. C. engine, 223
- Indicator cards, 49
 Indicator diagrams, Diesel engine, 223
 Otto engine, 223
- Infinite refrigerator, 57
 Infinite source, heat, 56
- Internal combustion engines, 218
 methods of computing efficiency, 222
- Internal combustion engine cycles, Diesel,
 218, 220, 221
 Otto, 218, 221
 pumping loss, 237
 theoretical analysis, 235
- Intrinsic energy (F), 23
 a function of temperature only, 130
 a point function, 24
 change for gases, 143, 144, 149, 152
 evaluation of ΔF , 136, 137, 138
 kinetic theory of, 24
 of wet vapor, 170
 value of, 42
- Inversion temperature, 133
 Irreversibility, mechanical and thermal, 80
 Irreversible adiabatic expansion, 75
 Irreversible cycles, 74
 Irreversible process, entropy change of, 79
 Isometric change, 38
 Isopiestic change, 38
 Isothermal change, 37
 Isothermal change of state of perfect gas, 143
 entropy change, 146
 evaluation of Q , W , and ΔF , 144
- J*, Joule's mechanical equivalent of heat, 23
 Joule, James Prescott, 3, 22, 129, 130, 131, 132
 Joule-Thomson coefficient, 132
 Joule-Thomson effect, 131
 Joule's experiment, 129
 Joule's Law, 129, 130
- k*, ratio of specific heats (c_p/c_v), 137
- Keenan, J. H., 162
 Kelvin, Lord, 4, 67
 Kelvin temperature scale, 13
 conversion, 14
- Keyes, F. G., 162
 Kinetic theory of intrinsic energy, 24
- Latent heat, 165
 defined, 17
 of evaporation, 17, 174
 of fusion, 17
- Latent heats, table of, 17
- Laws, Avogadro's, 112
 Boyle's, 105
 Charles', 106
 Gay Lussac's, 106
 ideal gas, 107, 109
 Joule's, 129, 130
 of Thermodynamics, 3, First, 3, 4, 14, 25,
 Second, 4, 65, 86, Third, 5, 97, 99
 perfect gas, 107
- Leet's characteristic equation for gases, 117
 Lenoir cycle and engine, 219
 Lewis, G. N., 99
 Linde process, 133
 Liquefaction of gases, Linde process, 133
 Liquid, saturated, 168
 Liquid line, 172, 174
 Lower fluid, binary cycle, 256
- Maximum work, 86
 and heat of reaction, 91
- Mayer, Robert, 3
 Mean effective pressure, 223
 Mechanical equivalent of heat, 22
 Medium, working, 5
 Mixtures, gaseous, 126
 apparent molecular weight, 127
 gas constant, 127
 specific heat, 127, 128

- Mol defined, 113
 Molecules, kinetic and potential energy of, 24, 25
 Mollier diagram, 176, 177
 Multi-stage compression, air, 209

 n (exponent), 39, 45, 106
 Nernst, 5, 99
 Non-flow change, constant pressure, 85
 constant volume, 84
 reversible adiabatic, 84
 Non-flow change of state of perfect gas, constant pressure, 140
 constant volume, 135
 isothermal, 143
 polytropic, 150
 reversible adiabatic, 146
 Non-flow process, 28
 energy equation, 36, 57
 Nozzle, turbine, efficiency, 264
 expansion of steam through, 263
 velocity coefficient, 264
 Nozzle efficiency, 264

 Olzewski, 133
 Otto cycle, 218-221
 air standard efficiency, 226
 diagram of ideal 4-stroke cycle, 226

 Parsons, Sir Charles, 247
 Path functions, 39
 Perfect gas, 106
 characteristic equation of, 108
 changes of state, adiabatic, 146; constant pressure, 140; constant volume, 135; isothermal, 143; polytropic, 150
 Perfect gas law, 107
 empirical adaptation, 119
 Permanent gases, 105
 Planck, 66
 Point, of cutoff, 260
 of release, 260
 Point functions, 39
 E (intrinsic energy), 93
 exact differential, 94
 F (free energy), 86, 88, 93
 H (enthalpy), 93
 S (entropy), 71, 74
 use in evaluating ${}_1Q_2$, and ${}_1W_2$, 83
 W_{\max} (maximum work), 86, 93
 Polytropic change of state, 38
 perfect gas, 150; entropy change, 156;
 specific heat (c_n), 153, 154
 water vapor, 187
 Porous plug experiment, 131
 Potential energy of a body, 10, 25
 Power, I. C. engine, brake, 223
 indicated, 223
 Power plant, steam, 240

 Pressure, defined, 10
 a thermodynamic coordinate, 9
 absolute, 11
 atmospheric, 11, 12
 coefficient (β) of, 110
 critical, 117, 118
 gage, 11
 mean effective, 223
 Pressure staging, impulse turbine, 267
 Process, constant pressure, 38
 constant volume, 38
 cyclical, 42
 non-flow, 28
 reversible, 53, 87
 steady flow, 27
 throttling, 132
 Properties, of gases, 105
 of vapors, 161, 162
 Pump, hotwell, 246
 Pumping loss, I. C. engine, 237

 Q , evaluation of, 42
 Quality (x) of steam, defined, 168
 determination of, 193

 R , gas constant, 112
 Radiation of heat, 21
 Stefan-Boltzmann Law, 21
 Randall, Merle, 99
 Rankine cycle, 241
 effect, of decreasing condenser temperature and pressure, 246, 247; of increasing boiler pressure, 249; of superheating, 248
 methods of improving efficiency, 246
 thermal efficiency, 243, 246
 work of, 243
 Rankine temperature scale, 13
 conversion, 14
 Ratio, of compression, 221
 of specific heats, $c_p/c_v = k$, 137
 Reaction turbine, 267
 Reciprocating steam engine, 257
 Refrigerator, infinite, 57
 Regenerative feed-heating cycle, 252
 Reheating cycle, 252, 254
 Release, point of, 260
 Reversibility, 53
 Reversible cycles, 74
 Reversible process, 53, 87
 Rumford, Count, 3

 Saturated liquid, 168, 172, 174
 Saturated vapor, 168, 172, 174
 Saturation line, 172, 174
 Second Law of Thermodynamics, 4, 65, 86
 Smith, L. B., 162
 Specific heat, 14
 at constant pressure, 15
 at constant volume, 15

- Specific heat (cont.)
 for polytropic change, 152, 153, 154
 of gaseous mixtures, 127
- Specific heats, ratio of $c_p/c_v = k$, 137
 table, 16
 variable, for gases, 120
- Specific volume, 12
- Steady-flow process, 27
 See also Vapor, water
- Steam, superheated, 171
- Steam cycles, 239
 binary, 252, 255
 ideal Rankine, 241
 incomplete expansion, 259
 regenerative feed heating, 252
 reheating, 252, 254
 reheating regenerative, 254
- Steam engines, 239
 expansion, complete, 258, incomplete, 259
 governing, 262
 mechanical elements of, 258
 non-expansion, 258
 reciprocating, 257
 throttling, 262
- Steam power plants, equipment, 240
 improvements in efficiency, 251
- Steam tables, 167, 274
 headings, 167
 physical and graphic representation, 172, 173
 research, 163
- Steam turbine nozzles, expansion through, 263
 nozzle efficiency, 264
 velocity coefficient, 264
- Steam turbines, 262
 impulse, 265
 pressure staging, 267
 reaction, 267
 types, 269
 velocity staging, 267
- Stefan-Boltzmann law, 21
- Stirling, Robert, 218
- Superheat, degree of, 172
 region of, 173, 174
- Superheated steam, 171, 174
- Superheating steam, effect in Rankine Cycle, 249
 enthalpy change, 174
- System, thermodynamic, 19
- Tables, constants for van der Waals' equation, 115
 critical properties of some substances, 118
 latent heats, 17
 non flow changes of state, of perfect gas, 157, of water vapor, 197
 specific heats, 16
 specific volume of simple gases, 112
 steam, 274
- Temperature, a thermodynamic coordinate, 9
 absolute, 13
 absolute zero of, 12
 conversion of scales, 8
 critical, 117, 118
 kinetic theory of, 25
 meaning of, 5
 measuring devices, 7
 of evaporation, 163
 of inversion, 133
 thermodynamic scale of, 62
- Temperature scales, comparison of centigrade, Fahrenheit, Kelvin, and Rankine, 13
- Thermal capacity, 14, 15
- Thermal efficiency, fundamental basis of, 59
 of I C. engine, 224
- Thermal irreversibility, 80
- Thermodynamic changes, adiabatic, 38
 isometric, 38
 isopiestic, 38
 isothermal, 37
 limiting types of, 37
 polytropic, 38
- Thermodynamic coordinates, 8
 enthalpy, 31
 entropy, 71
 pressure, 9
 temperature, 9
 volume, 9
- Thermodynamic properties, of gases, 105
 of vapors, 161
- Thermodynamic scale of absolute temperature, 62
- Thermodynamics, defined, 1
 First Law of, 3, 4, 19, 25
 general energy equation of, 28
 Second Law of, 4, 65, 86
 Third Law of, 5, 97, 99
- Thermometer, gas, 110
- Thermometers, scales of, 8
 types of, 7
- Thermometry, 6
- Third Law of Thermodynamics, 5, 97, 99
- Thomson, 131, 132
- Throttle valve, 190
- Throttling, Joule-Thomson effect, 131
 steam engine governing, 262
- Throttling calorimeter, 193
 limitations of, 194
- Throttling process, 132, 190
- Top Fuel, binary cycle, 256
- Transformation of energy, 19, 20
- Turbine nozzles, expansion of steam through, 263
 nozzle efficiency, 264
 velocity coefficient, 264

- Turbines, steam, 239, 262
 - classification of, 263
 - impulse, 265
 - impulse-pressure staging, 267
 - impulse-velocity staging, 267
 - mechanical elements of, 263
 - reaction, 267
 - types, 269
- Unavailable energy, 80
- Unavailable heat, 77
- Unit heat quantity, 14
- Units used with gas law equations, 111
- Universal gas constant (R), 113, 115
- Vacuum gage, 11
- van der Waals, 114
- van der Waals' Equation, 114
- Vapor, water, properties of, 162
 - saturated, 168
 - superheated, 174
 - wet, 168
- Vapor change of state, adiabatic, 186
 - constant enthalpy, 190
 - constant pressure, 180
 - constant volume, 178
 - isothermal, 182
 - polytropic, 187
- Vapor pressure and temperature, 166
- Vapors, change of state of, 161
 - characteristic equations of, 161
 - nature of, 161
 - thermodynamic properties of, 161
- Variable specific heat of gases, 120
- Velocity coefficient, 264
- Velocity staging, impulse turbine, 267
- Volume, critical, 117, 118
 - defined, 12
 - of wet vapor, 169
 - specific, 12
- Volume coefficient (α), 110
- Volume composition of gases, 126
- Volumetric efficiency, air compressor, 210
- W_2 (work), evaluation of, 43
- W_{\max} (maximum work), 86, 87
- Water jacketing, air compressor, 207
- Water vapor, 162
 - changes of state, adiabatic, 186; constant enthalpy, 190; constant pressure, 180; constant volume, 178; isothermal, 182; polytropic, 187
- Watt, James, 239, 258
- Weight composition of gases, 126
- Wet vapor, 168
 - enthalpy (h_x), 170
 - entropy (s_x), 170
 - intrinsic energy (e_x), 170
 - region of, 173, 174
 - volume (v_x), 169
- Work, and heat, 19
 - and mechanical energy, 22
 - defined, 22
 - evaluation of, 43
 - maximum, 86
 - of cyclical process, 48
 - of air compressor, 203, 204
- Working medium, 5
- x (quality of steam), 168
- Zero, absolute, 12, 13